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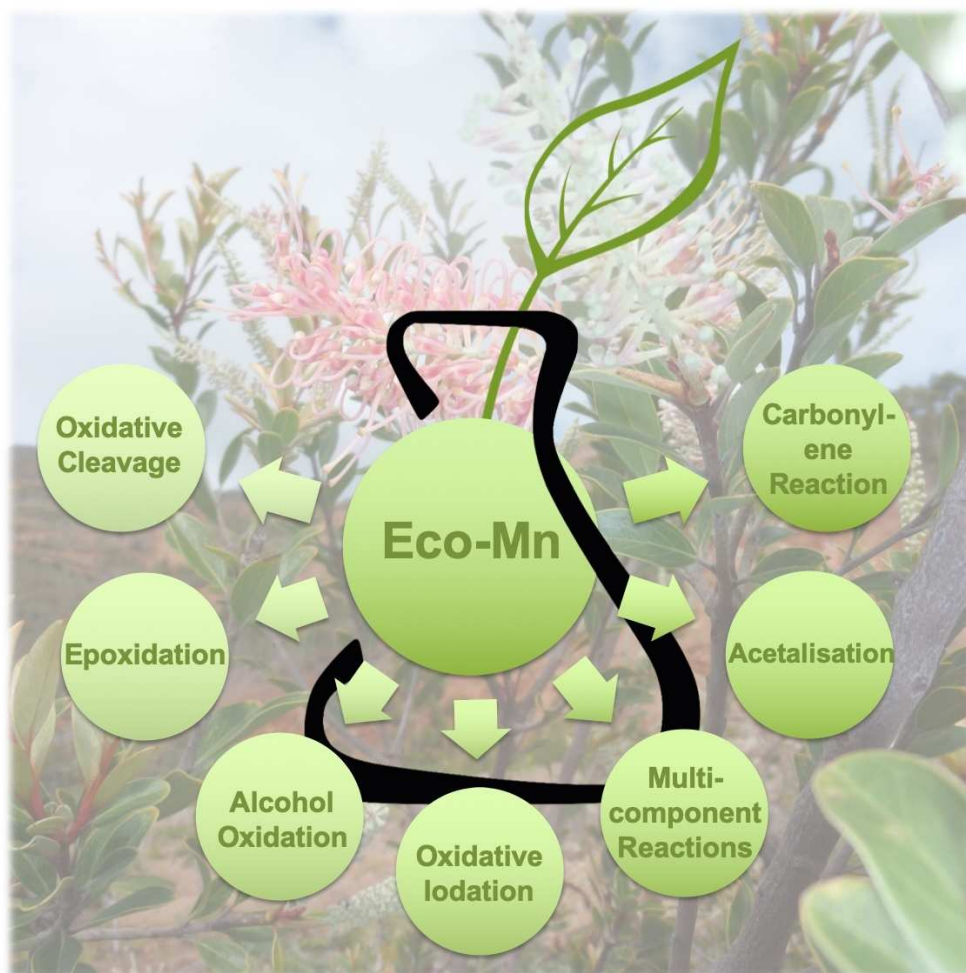
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Eco-Mn Ecocatalysts: Toolbox for Sustainable and Green Lewis Acid Catalysis and Oxidation Reactions

Camille Bihanic,^[a] Kenza Richards,^[a] Tomasz K. Olszewski,^[b] and Claude Grison^{*[a]}



Phytoextraction is one of the most promising phytotechnologies used to restore natural environments degraded by mining activities. In New Caledonia, a few plant species, which belong to the *Grevillea* genus, have the ability to extract Mn from soil and accumulate it in abundance (over 1 % of leaves dry weight). This review describes the use of *Grevillea* Mn-accumulating plant species to produce the first bio-sourced Mn catalysts, called Eco-Mn catalysts. Extensive structural studies of Eco-Mn

1. Introduction

The depletion of the world mineral resources has become a critical issue from economic and environmental points of view. Recycling techniques are still underdeveloped and the rising demand for metallic elements induces a short-term depletion of mineral resources. Access to strategic and primary minerals has become crucial considering this depletion, especially since these minerals are owned by a small number of politically unstable countries. In addition to having values for mining industries, transition metals, such as Mn, are essential for many chemical transformations in the fields of petrochemicals, agrochemicals, polymers, plastics, textiles, dyes, paints, drugs, cosmetics and perfumes. Recently it was reported that the short-term shortage of metal species used in catalytic chemistry is a major issue that chemical industries have now to face. For instance, Mn has been on the list of critical elements in the US since 2017. Referring to the currently known resources, Mn resources could be depleted in 20 to 50 years.^[1] The need of metallic elements induces the expansion of mining sites and the use of new extraction techniques, causing significant environmental issues: degradation of natural environments, loss of biodiversity and pollution of ecosystems.

The energy and ecological transition lead to a paradox. While the motives are those of environmental progress through the development of green energies, this transition underlies an increase in mineral resources requirement and ultimately a rising pressure on the demand for metals. The environmental consequences are worrying.

New Caledonia is a representative example of the global context and its current evolution. New Caledonia is an archipelago located in the South Pacific (20°–23° South, 164°–167° East).^[2] The ultramafic soils of New Caledonia are naturally enriched in valuable metallic elements, such as nickel, cobalt, manganese, iron, chromium and scandium,^[2,3] and nickel, particularly in laterite, represents one of the largest resources of nickel in the world.^[4] Access to metal deposits, located at a

catalysts have highlighted an original composition characteristic of their vegetal origin. Eco-Mn catalysts have demonstrated competitive catalytic activities compared to conventional Mn catalysts in Lewis acid catalysis, aminoreductions, alcohol oxidations, epoxidation reactions, oxidative cleavage of 1,2-diols and alkenes and “Janus catalysts” for sequential tandem oxidations such as tandem carbonyl-ene cyclisation, synthesis of substituted pyridines and oxidative iodination of ketones.

particular depth, requires the removal of the upper part of soil and hence the destruction of all vegetation cover, leading to serious ecological impacts for the island.^[5,6] Indeed, removal of the vegetation cover affects the biodiversity and the landscape environment. In addition, erosion and leaching of soils, denuded by prospecting and ore extraction, cause significant damages to ecosystems. The sediments are dragged away into rivers and then into the New Caledonian lagoon, a World Heritage site by UNESCO,^[7] thus threatening the coral reef surrounding the island.^[5,8]

In this context, our group has developed new rehabilitation programs on six mining sites of New Caledonia. Our approach is based on using the New Caledonian biodiversity and endemic pioneer plants that have naturally evolved to grow on ultramafic soils. Some of them are Ni- or Mn-(hyper)accumulating plants. (Hyper)accumulating plants are able to translocate metals from roots and store them into shoots (Figure 1).^[6,9–13] These plants are accommodated to multiple local constraints: open environment, tropical climate, edaphic and hydric constraints, high altitude, degraded soils depleted of nutrients and micro-organisms, and more interestingly adapt to soils rich in the toxic elements Ni, Co, Mn, Cr, Fe. Thus they are remarkably adapted to the impacts resulting from mining activities and are ideal plants to start the rehabilitation of degraded sites.^[14]

Among the pioneer Mn-accumulating plants, *Grevillea exul* ssp *exul* and ssp *rubiginosa*, *Grevillea meisneri* and *Grevillea gillivrayi* of the genus *Grevillea* were selected for restoration (Figure 2).^[15–18] The average foliar manganese concentration in normal plants is 2590 mg/kg (dry weight), which places *Grevillea exul* among the most Mn-rich species but without being an

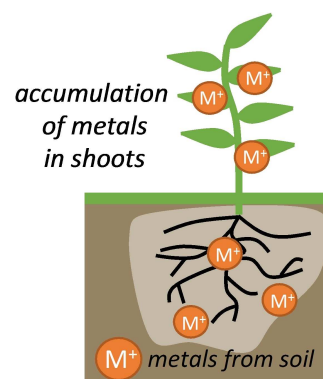


Figure 1. (Hyper)accumulation of metal elements from mining residues by plants.

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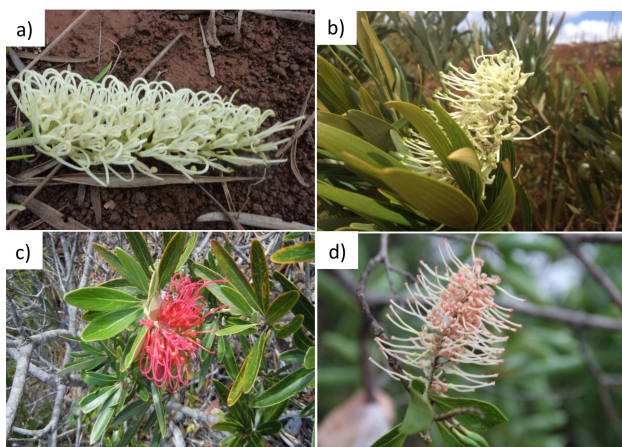


Figure 2. New Caledonian Mn-accumulators: a) *Grevillea exul ssp exul*; b) *Grevillea exul ssp rubiginosa*; c) *Grevillea meisneri* and d) *Grevillea gillivrayi*.

hyperaccumulator (threshold at 10 000 mg/kg). Individual measurements up to 3900 mg/kg have been reported for the variety *exul* and up to 6200 mg/kg for the variety *rubiginosa*.^[18,19]

These Mn-accumulating plants being particularly abundant in New Caledonia deserve a particular effort of conservation and make them ideal candidates for ecological restoration, in the strict sense of the term.

In 2009, our group showed that it was possible to combine ecological restoration and economic opportunities. Plants used for restoration were transformed through an innovative concept of recycling. Taking advantage of the remarkable adaptive capacity of some plants to accumulate manganese, we directly

use the metallic species, originated from this metal-rich biomass, as catalysts in fine organic chemistry. This original approach offered the first perspective of valorization of this unique biomass and initiated a new field of green chemistry: the ecocatalysis (Scheme 1).^[20-22]

The concept of ecocatalysis has allowed the preparation of a wide range of ecological catalysts: the ecocatalysts.^[23-27] Ecocatalysts present a flexible reactivity, while respecting the principles of Green chemistry. Ecocatalysts can be used as heterogeneous catalysts in synthetic transformations allowing access to molecules with a high added-value for the production of fine chemicals and in scalable processes.^[28,29] Among the different ecocatalysts prepared to date, Eco-Mn catalysts have two major properties:^[14,30] a hard and marked Lewis acidity or/ and an oxidative activity allowing the replacement of oxidants prohibited by REACH regulation (Registration, Evaluation, Authorization and Restriction of Chemicals) (European Commission 2006).^[31] These interesting properties are specific to Eco-Mn catalysts and are the consequence of a particular structure of these materials. The organization of their nanostructures is related to the nature of the plant species they derive from and to the unique and uncommon catalytic species generated during their preparation.^[32] In this review, we illustrate the synthetic potential of these new generations of catalysts, Eco-Mn catalysts, in which the transition metal, Mn, is purely bio-based.

The first chapter is dedicated to the Lewis acidity of Eco-Mn catalysts (called Eco-Mn_{LA}) shown by pyridine sorption capacity and applied to three chemical transformations: the carbonyl-ene cyclisation of citronellal, the enol ether synthesis and the amino-reduction of carbonyl derivatives. In a second chapter, the oxidative capacities of Eco-Mn catalysts (called Eco-Mn_{ox})



Claude Grison is CNRS Research Director. She is leading the Laboratory of Bio-inspired Chemistry and Ecological Innovations (Montpellier, France), which is dedicated to the implementation of new ecological solutions and innovative chemical tools for the ambitions of tomorrow's chemistry. C. Grison is the pioneer of the ecocatalysis concept, which represents a major break-through at the interface between ecology and chemistry. Author and co-author of more than 181 scientific articles and patents, she has received 9 Awards for Innovation.



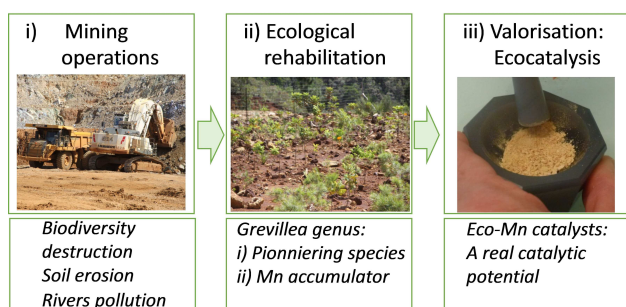
Tomasz K. Olszewski obtained his PhD degree in 2006 from Wroclaw University of Science and Technology (WUST), Poland (with Prof. Bogdan Boduszek) and from University of Montpellier, France (under the guidance of Prof. Claude Grison). After postdoctoral period and work in industry he returned to academia in 2012 and obtained habilitation in 2016. Currently, he holds position of Associate Professor at WUST. His research interests are focused on synthesis and applications of organophosphorus compounds and recently catalysis.



Camille Bihanic was graduated in Chemistry at Ecole Normale Supérieure of Lyon (France). She first joined the Laboratory of Bio-inspired Chemistry and Ecological Innovations (France) for her master internship in 2017 and is currently pursuing her PhD studies in the laboratory, under the supervision of Dr. C. Grison. Her doctoral research focus on the preparation of Mn-based ecocatalysts from accumulating plant species, used in ecological rehabilitation of New Caledonian mining sites.



Kenza Richards received her Green Chemistry Engineering degree from the ENSIACET and her Master's degree from the Université Paul Sabatier (Toulouse). She started her PhD in 2018 in Montpellier at the Laboratory of Bio-Inspired Chemistry and Ecological Innovations under the supervision of Pr. Claude Grison. Her research interests are focused on the ecological rehabilitation of degraded sites especially the metal decontamination of mining effluents through the mobilization of biomass, and the valorization of the latest by eco-catalysis.



Scheme 1. From the ecological rehabilitation of New Caledonian mining sites to an original valorization: Ecocatalysis.

are illustrated by major transformations used in the chemical industry: alcohol oxidation, diol oxidative cleavage, ketone iodization, aromatizing dehydrogenation and alkene epoxidation. A final chapter presents the Janus character of the Eco-Mn catalysts (called Eco-Mn_{LA-Ox}) in tandem sequences of multi-component-type reactions (synthesis of substituted pyridines) and cyclizations (synthesis of *p*-cymene).

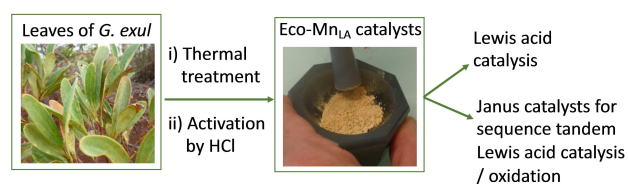
2. Preparation and characterization of Eco-Mn catalysts

2.1. Preparation of Eco-Mn_{LA} catalysts

A crucial feature of Eco-Mn catalysts is their polymetallic composition resulting from the combination of Mn²⁺ at high concentration with physiological elements of the plants (e.g. Fe³⁺, Na⁺, K⁺, Ca²⁺, Mg²⁺).

The preparation of Eco-Mn catalysts requires experimental conditions that allow us to control the composition, structure and degree of oxidation of Mn that modulate the subsequent reactivity. The key steps for the preparation of Eco-Mn are (i) heat treatment and (ii) activation by introduction of new anions (treatment with HCl). The heat treatment burns to ashes the organic material of plants and the acid treatment allows the solubilization of metals as metal chlorides. These experimental conditions generate ecocatalysts with Lewis acidity properties called Eco-Mn_{LA} (Scheme 2).

Eco-Mn_{LA} catalysts are polymetallic catalysts composed of a set of salts, including mixed salts (non-monometallic salts). Eco-Mn_{LA} catalysts are mainly composed of Ca, Mg, Na, K and Mn



Scheme 2. Experimental conditions for the preparation of Eco-Mn_{LA} catalysts.

cations, and contain Fe, Ni and Al cations in smaller amounts. Manganese is exclusively present in the oxidation state II in an octahedral environment; and iron is predominantly present in the oxidation state III in octahedral or tetrahedral environments depending on the catalysts. The anions of Eco-Mn_{LA} catalysts are chlorides due to the chemical treatment, but also of sulphates and phosphates due to the plant origin.

The compositions of Eco-Mn_{LA} catalysts vary according to the plants from which they derive, as illustrated by our study on *Grevillea* plants that were used in mining restoration.[19] However, the Mn content of Eco-Mn_{LA} catalysts is reproducible, about 4%, 5.5%, 6.5% and 11% for *Grevillea exul ssp exul*, *gillivrayi*, *exul ssp. rubiginosa* and *meisneri* respectively. It is directly linked to the accumulation capacities of each species (Table 1).[19]

We have extensively studied and characterized the crystal-line structure of Eco-Mn_{LA} and the chemical environment around active catalytic centers (manganese and iron) by X-Absorption Spectroscopy (EXAFS and XANES) analyses. We found that Eco-Mn_{LA} catalysts are not a juxtaposition of simple metal chlorides, but that their composition is much more complex. Unusual and mixed metal chlorides, such as K₃NaMnCl₆ and KMnCl₃, were clearly identified and were further crystallized for an identification by XRD (Figure 3).[32] To a lesser extent, iron and magnesium are also present as a mixed metal chlorides K₂FeCl₅H₂O,^[32] and KMgCl₃·6H₂O.^[33]

We also demonstrated that Eco-Mn_{LA} catalysts cannot be reproduced, in terms of structure, properties and catalytic activities, by mixtures of commercial metallic salts or by mixing any biomass with a manganese salt. This study highlighted the peculiar vegetal footprint of Eco-Mn catalysts.

This conclusion can be generalized to all Eco-Mn_{LA} derived from plant species of the genus *Grevillea* used in mining

Table 1. Composition of leaves of *Grevillea* and derived Eco-Mn_{LA} catalysts determined by ICP-MS analysis.

	Physiological metals [wt %]					Accumulated metals [wt %]		
	Na	Mg	Al	K	Ca	Fe	Mn	Ni
Leaves <i>Grevillea exul ssp. rubiginosa</i>	0.12	0.24	0.02	0.44	0.24	0.05	0.40	0.01
Eco-Mn _{LA1} <i>Grevillea exul ssp. rubiginosa</i> HCl 12 M	0.81	5.44	0.29	3.79	7.86	0.72	6.46	0.20
Leaves <i>Grevillea exul ssp. exul</i>	0.05	0.18	0	0.71	0.86	0.12	0.21	0.01
Eco-Mn _{LA2} <i>Grevillea exul ssp. exul</i> . HCl 12 M	0.58	3.27	0.17	9.87	9.98	2.77	3.99	0.26
Leaves <i>Grevillea gillivrayi</i>	0.12	0.31	0.05	0.27	1.15	0.24	0.36	0.06
Eco-Mn _{LA3} <i>Grevillea gillivrayi</i> . HCl 12 M	0.61	4.96	0.22	3.11	9.99	2.16	5.51	0.09
Leaves <i>Grevillea meisneri</i>	0.14	0.12	0	0.27	0.80	0.06	0.67	0.03
Eco-Mn _{LA4} <i>Grevillea meisneri</i> HCl 12 M	0.84	2.01	1.16	3.93	12.54	0.37	11.71	0.04



Figure 3. Crystal of two mixed metal chlorides: a) KMnCl_3 and b) $\text{K}_3\text{NaMnCl}_6$ from $\text{Eco-Mn}_{\text{LA}}$ identified by XRD analyses.

restoration: *Grevillea exul* ssp. *rubiginosa*, *Grevillea exul* ssp. *exul*, *Grevillea meisneri* and *Grevillea gillivrayi*.^[32]

2.2. Preparation of $\text{Eco-Mn}_{\text{OX}}$ catalysts

Our group has established a general procedure for the preparation of $\text{Eco-Mn}_{\text{OX}}$ catalysts from $\text{Eco-Mn}_{\text{LA}}$ catalysts, that are treated with a green co-oxidant (H_2O_2 or O_2) (Scheme 3). According to the co-oxidant used and the experimental conditions, the catalytic properties differ.

We reported three catalytic systems:

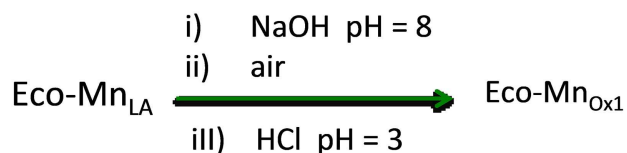
- $\text{Eco-Mn}_{\text{OX1}}$: $\text{Eco-Mn}_{\text{LA}}$ is oxidized by the oxygen from air at atmospheric pressure and at pH 8. Mn(II) is oxidized into Mn_2O_3 (Mn(III)) and Mn_3O_4 (Mn(II, III)). Fe(III) also present in $\text{Eco-Mn}_{\text{LA}}$ catalysts precipitates as Fe_2O_3 .

Mn_2O_3 (Mn(III)) and Mn_3O_4 (Mn(II, III)) are then transformed by disproportionation into soluble Mn^{2+} ions (Mn(II)) and MnO_2 (Mn(IV)) in acid conditions at pH=3. After acidification, Fe_2O_3 is also converted to soluble hydrated iron chloride ions. The final mixture is composed of MnO_2 , Mn(II) and Fe(III) chlorides, which can all act as Lewis acids (Scheme 4).^[34]

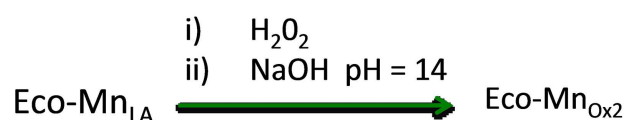
- $\text{Eco-Mn}_{\text{OX2}}$: $\text{Eco-Mn}_{\text{LA}}$ is oxidized by hydrogen peroxide in the presence of a large excess of sodium hydroxide. The precipitate formed is composed of a mixture of Mn oxides: $\text{Na}_{0.55}\text{Mn}_2\text{O}_4 \cdot 1.5\text{H}_2\text{O}$, $\text{MnO}(\text{OH})$, Mn_3O_4 and CaMn_3O_8 (Scheme 5).^[35]

- $\text{Eco-Mn}_{\text{OX3}}$: $\text{Eco-Mn}_{\text{LA}}$ is supported on montmorillonite K10, then added to the substrate and treated by a mixture of sodium bicarbonate and hydrogen peroxide (Scheme 6).^[36]

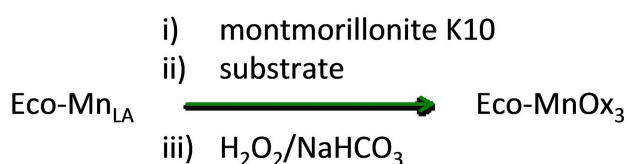
If the experimental conditions allow the preservation of all the metallic elements of $\text{Eco-Mn}_{\text{LA}}$, it is not true for $\text{Eco-Mn}_{\text{OX}}$.



Scheme 4. Experimental conditions for the preparation of $\text{Eco-Mn}_{\text{OX1}}$ catalysts.



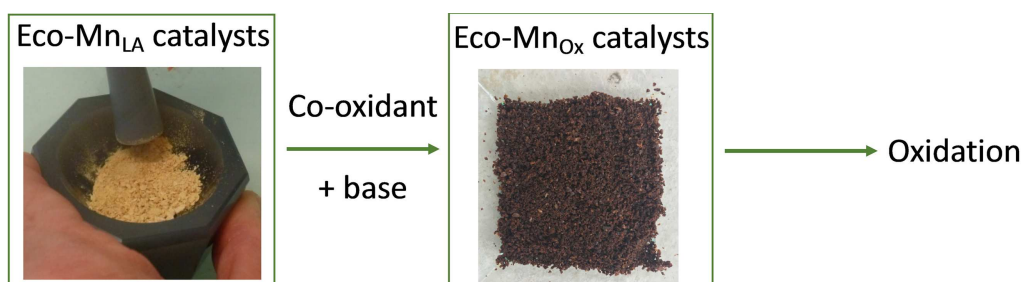
Scheme 5. Experimental conditions for the preparation of $\text{Eco-Mn}_{\text{OX2}}$ catalysts.



Scheme 6. Experimental conditions for the preparation of $\text{Eco-Mn}_{\text{OX3}}$ catalysts.

Table 2 illustrates the metallic compositions of $\text{Eco-Mn}_{\text{LA}}$ catalysts and $\text{Eco-Mn}_{\text{OX2}}$ catalysts.^[35] The treatment eliminates 2/3 of the Fe present in $\text{Eco-Mn}_{\text{LA}}$ in favor of a higher rate of Mn. The polymetallic nature of the ecocatalyst is however preserved with an interesting mixture of Mn/Ca/Mg.

Regardless of the preparation of Eco-Mn , its composition is polymetallic and the nature of the species formed is known. The simultaneous presence of a combination of well-defined active sites results from this variety of metallic species. A conventional catalyst would influence only some of the reaction process steps, thus limiting opportunities in organic synthesis. Here, the richness of the different interactions between the species present in Eco-Mn leads to unusual metal/substrate



Scheme 3. Experimental conditions for the preparation of $\text{Eco-Mn}_{\text{OX}}$ type catalysts.

Table 2. ICP-AES analysis of Eco-Mn_{ox} compared to the starting Eco-Mn_{LA1}.

	Physiological metals [wt %]				Accumulated metals [wt %]	
	Mg	Ca	Al	Fe	Mn	Ni
Eco-Mn _{LA1}	5.26	10.44	0.24	0.90	6.72	0.04
Eco-Mn _{ox1}	0.71	2.85	0.78	6.79	48.22	0.35
Eco-Mn _{ox2}	28.70	28.20	0	0.30	14.10	0.30
Eco-Mn _{ox3} ^[a]	0.70	0.20	6.00	0.65	0.11	0

[a] Eco-Mn_{ox3} is supported on K10 montmorillonite.

interactions that is illustrated with functional transformations of high interest in organic synthesis.

3. Reactivity of Eco-Mn catalysts

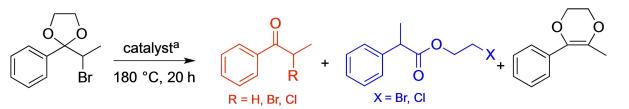
3.1. Catalysis by Eco-Mn_{LA} catalysts

The Lewis or Brønsted acid character of the eco-catalysts was demonstrated by studying their reactivity towards the cyclic acetal derived from α -bromopropiophenone and the selectivity of the formed products (Scheme 7). This technique is inspired from Corma's works that were on supported palladium and zinc catalysts.^[37,38] Eco-Mn_{LA} showed a hard Lewis acid character (43% yield of the hard Lewis acid products), and a marked Brønsted acidity (18% yield of the Brønsted acid products) and a negligible soft Lewis acidity (Scheme 7). The hard Lewis acidity is expected and explained by the presence of hard cations,^[39,40] and the Brønsted acidity might be due to the presence of iron in Eco-Mn_{LA} (0.7 wt% to 2.8 wt%).

These acid properties were explored through the carbonyl-ene cyclisation of citronellal, the synthesis of enol ethers and the reductive amination of carbonyl derivatives.

3.1.1. Carbonyl-ene cyclisation of citronellal^[34]

Carbonyl-ene cyclisation of (+)-citronellal into (-)-isopulegol is the key step of the synthesis of (-)-menthol, which is one of



	Conversion ^b	Brønsted acid sites ^c	Hard Lewis acid sites ^c	Soft Lewis acid sites ^c
Eco-Mn _{LA}	62	29	69	2
MnCl ₂	20	14	72	14
MnCl ₂ ·4H ₂ O	7	71	0	29
FeCl ₃	100	3	97	0
FeCl ₃ ·6H ₂ O	100	15	85	0

Scheme 7. Conversion rates and selectivity of products from the rearrangement of ethylene acetal of 2-bromopropiophenone with commercial manganese or iron chlorides and with Eco-Mn. ^a Reaction conditions: 2-bromopropiophenone (0.29 mmol), catalyst (4 mol%), water (0.29 mmol), 1,2-dichlorobenzene (3.3 mL), 180 °C, 20 h. ^b Determined by GC-MS analysis. ^c Ratio of yield to conversion as a percentage.

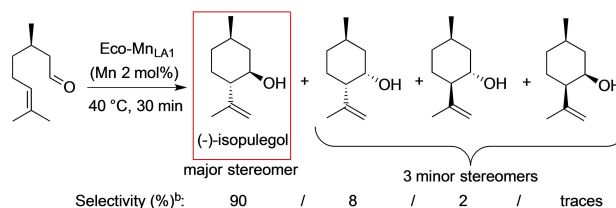
the most used flavoring chemicals.^[41,42] Since the skeleton of the (-)-isopulegol has two new stereogenic centers relative to (+)-citronellal, the intramolecular carbonyl-ene reaction can lead to four diastereomers.^[43] The (-)-isopulegol is the only isomer of industrial interest.

The synthesis of (-)-isopulegol from (+)-citronellal requires a high diastereoselectivity. The carbonyl-ene cyclisation of (+)-citronellal into (-)-isopulegol is favored by Lewis acids,^[44] while the use of Brønsted acid leads to lower selectivity of (-)-isopulegol.^[45,46] The selectivity of this cyclisation is directly related to the strength and hardness of Lewis acid metal centers. The Mn²⁺ cation is a Lewis acid of ideal hardness, but its use is limited by its low reactivity for this reaction. The polymetallic composition of Eco-Mn_{LA} and the presence of cations such as Fe³⁺ and Al³⁺ exalts the classical reactivity of Mn-based species. Eco-Mn_{LA} catalyzes the carbonyl-ene reaction, with 95% yield and 90% selectivity in the desired (-)-isopulegol, with only 2 mol% of Mn in a very short reaction time (0.5 h) (Scheme 8).

3.1.2. Enol ether synthesis^[34]

Alkyl enol ethers are of great synthetic interests. They are very reactive towards electrophilic reagents, in particular carbonyl groups, and are used for the formation of C–C bonds in organic synthesis. Compared to their metal enolate counterparts, alkyl enol ethers are more stable and can often be isolated. Alkyl enol ethers are also widely used in cycloaddition reactions, such as the inverse electron demand Diels-Alder reaction.^[47,48] Several literature reports about the preparation of alkyl enol ethers and their synthetic applications are available.^[49–51] Notable examples of compounds synthesized with the use of alkyl enol ethers include β -carotene, retinal (vitamin A aldehyde) and its derivatives,^[52,53] pyrrolidine alkaloids,^[54] iridodial natural products^[47] and tetrahydroquinoline derivatives,^[55] all having potential biological activity.

Conventional methods for the preparation of alkyl enol ethers involve the use of hard conditions such as strong bases (for example, *n*-butyllithium [*n*-BuLi], lithium diisopropylamide [LDA], sodium hydride) in toxic organic solvents (e.g., tetrahydrofuran, dichloromethane).^[50,56,57] However, it is also possible to synthesize alkyl enol ethers from aldehydes, by acetalization with an alcohol under acid catalysis, then removal of the



Scheme 8. Carbonyl-ene cyclisation of (+)-citronellal into isopulegol catalyzed by Eco-Mn_{LA}. Reaction conditions: Eco-Mn_{LA1} (2 mol%), dichloromethane, 40 °C, 30 min. ^b Determined by GC-MS analysis, ratio of yield to conversion as a percentage.

alcohol, under acid or base catalysis.^[58] The elimination step is generally carried out with the use of aggressive Brønsted acids, such as sulfuric acid or *p*-toluenesulfonic acid^[58] or readily hydrolysable Lewis acids, such as aluminum.^[59] This step can also be accomplished by co-catalysis with aluminum chloride and a non-nucleophilic base, such as triethylamine.^[59] Noticeably, none of these conditions are in accordance with the principles of green chemistry.

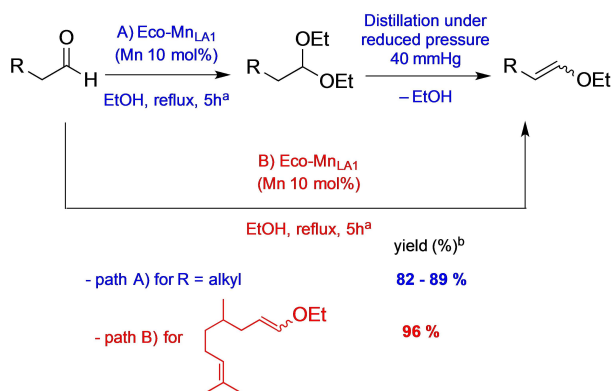
Given the double acid nature of Eco-Mn_{LA1} as hard Lewis and Brønsted acids, the formation of ethyl enol ether from carbonyl derivatives is possible (Scheme 9). Aliphatic aldehydes were treated with 10 mol% of Mn in anhydrous ethanol at 80 °C and lead to aliphatic acetals (path A) in good yields (77%–96%). The alcohol elimination of the acetals was performed by distillation and led to the corresponding ethyl enol ethers in good yields (82%–89%). When citronellal was used as substrate (path B), the corresponding enol ether was directly obtained and with a good yield (96%); no trace of acetal was detected. The conversion of the intermediate acetal was facilitated by the double Lewis and Brønsted acidity of Eco-Mn_{LA1} catalyst.

Eco-Mn_{LA1} catalyst has proved to be a green alternative to conventional acid catalysts used for the synthesis of enol ethers, avoiding the use of strong acid catalysts or sensitive reagents.

3.1.3. Reductive amination of ketones^[60]

Amines are very important industrial organic compounds that have found widespread applications in the pharmaceutical, agrochemical, material and chemical industries.

Reductive amination is one of the most common methods to prepare amines from carbonyl compounds in the presence of a reducing agent. Stoichiometric boron hydrides and heterogeneous hydrogenation have been mainly used to reduce reaction intermediates. However, the use of borohydrides generates abundant and hazardous wastes and heterogeneous hydrogenation is limited by its relatively poor chemoselectivity.^[61] An alternative method is based on the use of 1,4-dihydropyridines



Scheme 9. Acetalization/elimination of aldehydes catalyzed by Eco-Mn_{LA1}.^a Reaction conditions: aldehyde (1.0 mmol), Eco-Mn_{LA} (82 mg, amount corresponding to 10 mol% of Mn), anhydrous ethanol (3 mL), 80 °C, 5 h. ^b Yields were determined by GC-MS after calibration, using biphenyl as internal standard.

(DHP) and conducts to a competitive regio- and enantioselectivity compared to classical methods.^[62] DHP are hydride-donating agents in this reaction^[63] as they behave as biomimetic reducing agents of nicotinamide adenine dinucleotide (NADH). Commonly available 1,4-dihydropyridines are the Hantzsch esters (HEH). The reductive amination with HEH requires an acid promotor to activate the imine or ketiminium intermediates. Dry Mg(ClO₄)₂ and zinc ions are particularly effective.

The reductive amination is usually applied to aldehydes by using hazardous reductive agents. Using Eco-Mn_{LA1} catalysts, the reductive amination was applied to less reactive ketones in milder conditions respecting the principles of Green chemistry. The reaction was conducted under solvent-free conditions and with an easy to prepare, soft and non-toxic HEH.^[64]

The catalytic efficiency of the Eco-Mn_{LA1} catalyst was compared to conventional Mn chloride salts, which constitute the majority of the anions in Eco-Mn_{LA1} structure (Table 3). To highlight the differences between catalysts, the reaction was carried out with the poorly reactive 3-methyl-2-butanone. The use of Eco-Mn_{LA1} catalyst led to a higher conversion than commercial Mn chlorides, illustrating the original properties of the polymetallic complexes present in the plant-derived catalyst. This was confirmed by using a “reconstituted Eco-Mn_{LA1}” catalyst, prepared by mixing together commercial chlorides of K, Mg, Ca, Al, Mn, Fe and Ni, in the same proportions as the ones in Eco-Mn_{LA} catalyst. The reconstituted Eco-Mn_{LA1} catalyst behaved similarly to the original Eco-Mn_{LA1} catalyst. The catalytic performance of Eco-Mn_{LA1} catalyst is therefore specific to its particular polymetallic composition induced by its plant origin.

The reductive amination by Eco-Mn_{LA} was extended to various ketones using aliphatic and cyclic amines (Table 4). Eco-Mn_{LA} catalyst showed a high catalytic efficiency, since only 0.25 mol% of catalyst allowed 96% yield for the model reaction with cyclohexanone and aniline. Interestingly, the aliphatic and

Table 3. Reductive amination of ketones – comparison of Eco-Mn_{LA1} with classical Mn chlorides.^[a]

Entry	Catalyst	Catalyst loading [mol%] ^[b]	Yield [%] ^[c,d]
1	Eco-Mn _{LA1}	1	67
2	MnCl ₂	1	49
3 ^[e]	“reconstituted” Eco-Mn _{LA1}	1	62

[a] Reaction conditions: 3-methyl-2-butanone (1 mmol), aniline (1 mmol), HEH (1.1 mmol), neat, 110 °C, 4 h. [b] Eco-Mn_{LA} and “reconstituted” Eco-Mn_{LA} loadings calculated in Mn mol%. [c] Yields were determined by GC-MS after calibration, using biphenyl as an internal standard. [d] In all cases, less than 5% of residual imine were detected. [e] “Reconstituted” Eco-Mn_{LA} prepared by mixing commercial chlorides of K, Mg, Ca, Al, Mn, Fe and Ni, in the same proportions than in Eco-Mn_{LA}, according to its ICP-MS analysis. [f] 0.83 μL of 12 M HCl_(aq) were added (1 mol% of HCl).

Table 4. Reductive amination of ketones catalyzed by Eco-Mn_{LA}/HEH system – substrate scope.^[a]

Entry	Ketone	Amine	Product	Yield [%] ^[b]
1		Aniline		97
2		Aniline		67
3		Alkyl amines Aryl amines Cycloalkyl amines		96 95–99 96
4		Alkyl amines Aryl amines Cycloalkyl amines		96 38–67 95
5		Aniline		79
6		Aniline		67

[a] Reaction conditions: ketone (1 mmol), amine (1 mmol), HEH (1.1 mmol), Eco-Mn_{LA} (1 mol%) (calculated in Mn mol%), neat, 110 °C, 4 h. [b] Yields were determined by GC-MS after calibration, using biphenyl as an internal standard.

cyclic amines can also react with ketones under similar conditions and the desired products are formed in very good yields (88–96%, Table 4, entries 3). Using a cyclic ketone, the amino partner can be aniline substituted with electron withdrawing or donating groups (95–99%). The methodology was applied to the preparation of amines derived from 2-tetralone and 2-indanone as precursors of pharmaceutically compounds (Table 4, entries 5 & 6).

The Eco-Mn_{LA1} catalyst has been successfully used in the reductive amination of various ketones in combination with a non-toxic, affordable, and safe reducing agent, under a solvent-free methodology and in short reaction times (1–4 h). This illustrates well the capacity of Eco-Mn_{LA1} for the synthesis of substituted amines, including precursors of pharmaceutically compounds.

3.2. Catalysis by Eco-Mn_{Ox} catalysts

3.2.1. Eco-Mn_{Ox1} catalyst, a versatile oxidative agent of alcohols^[34]

The oxidation of benzylic alcohols to aldehydes is an important industrial chemical reaction. Many oxidizing agents are available to perform this key reaction. Although several stoichiometric reagents based on activated dimethylsulfoxide (Swern oxidation),^[65] hypervalent iodine compounds (Dess-Martin periodinane)^[66] and reactive oxo-metallic compounds (MnO₂ and pyridinium chlorochromate)^[67] have been developed. The search for new catalytic procedures for selective oxidation of benzyl or allylic alcohols remains an area of intense interest. Indeed, despite their efficiency, the disadvantage of the above-mentioned oxidants in the perspective of their use in multi-step synthesis is their lack of selectivity. For example, the over-oxidation of aldehydes to carboxylic acids and the degradation of unsaturated substrates are often unavoidable side reactions.

The oxidative potential of Eco-Mn_{Ox1} was first tested using benzyl alcohol (Table 5). Using less than 4 molar equivalents of Mn, Eco-Mn_{Ox1} catalyzed quantitatively the formation of benzaldehyde, while MnO₂ could not (Table 5, entry 1 & 2). The amounts of Mn species were quite small compared to conventional conditions (typically 10 equivalents).^[68] The polymetallic composition of Eco-Mn_{Ox1}, in particular the presence of Fe(III) species, increases the oxidizing properties of Mn(IV) while driving the reaction to the expected aldehyde. Indeed, only 20% of benzaldehyde was obtained using a mixture of MnO₂ and FeCl₃ (Table 5, entry 4). The combination of Mn(IV) and Fe(III) cannot explain the quantitative yield when using Eco-Mn_{Ox1}. We assumed a synergetic effect between the metallic species within Eco-Mn_{Ox1} or a specific structure of the catalyst due to its vegetal origin.^[32]

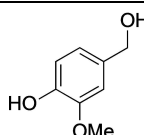
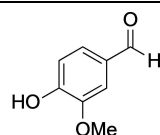
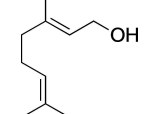
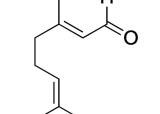
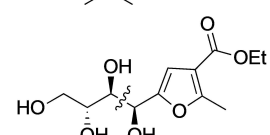
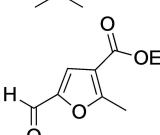
The absence of benzoic acid among the reaction products is an important advantage of the presented procedure. It was applied to the oxidation of 4-hydroxy-3-methoxybenzyl alcohol (vanillyl alcohol) to vanillin, which was quantitatively catalyzed by Eco-Mn_{Ox1} (Table 6, entry 1). It is noteworthy for an industrial development that this synthesis is entirely bio-based: the alcohol is a natural and abundant substance present in

Table 5. Oxidation of alcohols – comparison of Eco-Mn_{Ox1} with classical Mn oxides.^[a]

Entry	Catalyst	Catalyst loading [eq.]	Yield [%] ^[b]
1	Eco-Mn _{Ox1}	3.9	100
2	MnO ₂	3.9	traces
3 ^[68]	MnO ₂	10	89
4	MnO ₂ + FeCl ₃ ^[c]	3.9	20

[a] Reaction conditions: alcohol (10 mmol), catalyst (38.9 mmol Mn), EtOAc (20 mL), 75 °C, 3 h. [b] Yields were determined by GC-MS after calibration, using biphenyl as internal standard. [c] 5.30 mmol of FeCl₃ were used, in order to reproduce the ratio Mn/Fe of Eco-Mn_{Ox1}.

Table 6. Oxidation of alcohols by Eco-Mn_{Ox1}.^[a]

Entry	Alcohol	Catalyst	Product	Yield [%] ^[b]
1		Eco-Mn _{Ox1}		100
2		Eco-Mn _{Ox1}		100 ^[c]
3		Eco-Mn _{Ox1} ^[d]		100

[a] Reaction conditions: alcohol (10 mmol), catalyst (38.9 mmol Mn), EtOAc (20 mL), 75 °C, 3 h. [b] Yields were determined by GC-MS after calibration, using biphenyl as internal standard. [c] > 95% *trans*-citral was obtained. [d] Eco-Mn_{Ox1} (60 mmol).

numerous plant species such as *Picea sitchensis* (Pinaceae);^[69] the oxidant is completely natural, since it derives from *Grevillea exul rubiginosa*. This synthesized vanillin can be described as a natural aroma of vanillin.^[70]

The oxidation procedure was easily transposable to the controlled oxidation of allyl alcohols under similar conditions; for example, geraniol led to geranial (*trans*-citral) (Table 6, entry 2). This molecule faces a strong demand for its lemon scent in the food industry or as an important intermediate for the production of perfumes and pharmaceuticals.^[71]

The particular case of the polyhydroxyalkyl furan allowed to evaluate the chemoselectivity of the oxidation process catalyzed by Eco-Mn_{Ox1} (Table 6, entry 3). The furan aldehyde was obtained directly and in a quantitative yield. This result reflects the ability of Eco-Mn_{Ox1} to promote the oxidative cleavage of a polyol in the benzylic position. The reaction showed no concurrent side reaction, which confirmed the excellent regioselectivity of the cleavage. The yield of the reaction is remarkably higher with Eco-Mn_{Ox1} than with Ce(IV) reagents, which require a large excess of oxidant (11 equivalents, 48% yield).^[72] This oxidative cleavage of polyhydroxyalkyl furan to furan aldehyde could be an interesting way to produce functionalized furfural compounds, with new functionalities compared to the widely studied furfural compounds.^[73,74]

This method can easily replace toxic or unstable oxidants such as NaIO₄, Pb(OAc)₄, NaBiO₃, sodium and calcium hypochlorite, Ce(IV), Cr(VI), Co(II) or V(IV) reagents, *N*-iodosuccinimide.^[75] In addition, it can also be advantageously compared to recent methods using O₂ as an oxidant with ruthenium catalysis,^[76] palladium^[77] or cobalt.^[78] Although these methods represent valuable ecological improvements in the oxidative cleavage of glycols, the catalysts involved rely on rare and expensive metals, which considerably limit their use.

3.2.2. Selective aerobic oxidative cleavage of activated 1,2-diols catalyzed by Eco-Mn_{Ox2} catalyst^[35]

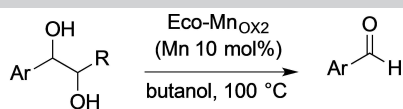
The catalytic properties of EcoMn_{Ox2} were also evaluated in the aerobic oxidative cleavage of 1,2-activated diols under atmospheric pressure of O₂ and with 10 mol% of Mn. A study of the solvent effect was carried out on *meso*-hydrobenzoin as a model substrate (Table 7). Almost complete conversion was obtained in 1 h in 1-butanol at 100 °C (98%, Table 7, entry 2). Complete selectivity for benzaldehyde was observed, with no traces of benzoic acid or other oxidation by-products. This result clearly contrasts with previous work on MnO₂, which requires 40 equivalents of Mn in dichloromethane.^[79]

Eco-Mn_{Ox2} was recovered by simple filtration after reaction and reused up to 6 times without any loss of activity. The E-factor of this reaction using EcoMn_{Ox2} shows that 4 to 17 times

Table 7. Solvent screening for EcoMn_{Ox2}-catalysed oxidative cleavage of *meso*-hydrobenzoin.

Entry	Catalyst	Solvent	T [°C]	Conversion [%] ^[b]
1 ^[a]	EcoMn _{Ox2} (10 mol%)	acetonitrile, ethyl acetate, toluene, water, ethanol, acetic acid	78	35–61
2 ^[a]	EcoMn_{Ox2} (10 mol%)	1-butanol	100	98

[a] Reaction conditions: *meso*-hydrobenzoin (0.2 mmol), Eco-Mn_{Ox2} (10 mol% Mn), 1 mL of solvent, O₂ balloon, 1 h. [b] Conversion was determined by GC-MS after calibration, using dodecane as internal standard.

Table 8. Scope of the aerobic oxidative cleavage of 1,2-diols catalyzed by EcoMn_{Ox2}.^[a]

R = Me, Ar
Ar: aryl, heteroaryl, cinnamyl

Entry	Substituent (R)	Conversion [%] ^[b]	Selectivity [%] ^[b,c]
1	Aryl, heteroaryl, cinnamyl	54–98	99
2	Methyl	57	99

[a] Reaction conditions: substrate (0.2 mmol), EcoMn_{Ox2} (10 mol% Mn), 1-butanol (1 mL), O₂ balloon, 100 °C. [b] Conversion, yield and selectivity were determined by GC-MS after calibration, using dodecane as internal standard; [c] Ratio of yield to conversion as a percentage.

Table 10. Eco-Mn_{Ox3} catalyzed epoxidation of styrene - solvent optimization.^[a]

Entry	Solvent	Conversion [%] ^[b]	Yield [%] ^[b]	Selectivity [%] ^[b,c]
1	DMF	95	85	89
2	1,2-propylene carbonate	4	4	100
3	acetonitrile, dichloromethane, water, isopropanol, 4-methyl-2-pentanol, glycerol, ethanol, THF, acetone, 2-butanone	< 20	< 20	63–100

[a] Reaction conditions: styrene (0.25 mmol), H₂O₂ (30 wt%) (0.8 mmol), NaHCO₃ (0.2 M) (0.05 mmol), supported Eco-Mn_{Ox3} catalyst (72 mg, Mn 0.58 mol%, Fe 3.35 mol%), solvent (2 mL), 0 °C, 4 h. [b] Conversion and yield were determined by GC-MS after calibration, using biphenyl as internal standard. [c] Ratio of yield to conversion as a percentage.

less wastes were generated compared to conventional systems, NaIO₄ or Pb(OAc)₄ respectively.

Other substrates were tested and complete conversions were obtained on activated benzyl and allyl diols, with excellent selectivities towards corresponding aldehydes or ketones (98–99%) and only 10 mol% of Mn, (Table 8). Among the diols studied, the superoxidized products, as carboxylic acids, were not detected.

3.2.3. Switchable alkene epoxidation/oxidative cleavage catalyzed by Eco-Mn_{Ox3} catalyst^[36]

Eco-Mn_{Ox3} catalyst is an unusual polymetallic complex of Mn(II) and Fe(III). Eco-Mn_{Ox3} was incorporated in Montmorillonite K10 giving a supported catalyst that was used to catalyze the epoxidation of alkenes with a mixture of H₂O₂ (30% w/w)/NaHCO₃ (0.2 M) as a green terminal oxidative reagent.

The supported Eco-Mn_{Ox3} catalyst presented a high efficiency for the epoxidation of styrene using a much lower Mn content than previously described heterogeneous Mn catalysts (Table 9, entry 1).^[84] On the contrary, Montmorillonite K10 alone and Eco-Mn_{LA1} did not result in the formation of the desired product (Table 9, entries 4 and 5). Inspired by the work of Richardson *et al.*,^[80] the addition of water into the reaction was

tested and resulted in a quantitative conversion of styrene with a reduced loading of Eco-Mn_{Ox3} catalyst (Mn 0.31 mol%, Fe 1.82 mol%, Table 9, entry 3) and a reduced quantity of the eco-unfriendly DMF.

The solvent classically used in this reaction is DMF, which is not recommended in green chemistry. An alternative solvent was investigated (Table 10), but DMF remains the best solvent for this reaction; all the other tested solvents led to conversions under 20%. Even using 1,2-propylene carbonate, which has been described as an environmentally friendly alternative to DMF,^[81] only 4% conversion was obtained (Table 10, entry 2).

Eco-Mn_{Ox3} can be recycled by simple filtration up to four times with less than 10% loss of Mn and no loss for Fe. The conversion and the yield remained unchanged after the fourth run, indicating a high stability of the Eco-Mn_{Ox3} catalyst (Table 11).

The scope of the method was extended to various alkenes, including complex natural products. Yields of epoxidation were mostly high (up to 99%) and sometimes higher than those described with conventional Mn-catalysts as Mn(II)-zeolite (Table 12).^[82]

The use of norbornene confirmed the effectiveness of the method with a yield of 99% of epoxy-norbornene (Table 12, entry 1). The reactions on (*R*)-(+)-limonene and citral (Table 12, entries 2 and 5) indicated that the electron rich double bonds are selectively epoxidized. Moderate activity was noted in the

Table 9. Epoxidation of styrene – comparison of Eco-Mn_{Ox3} with conventional catalysts.^[a]

Entry	Catalyst	Amount of Mn [mol %]	Amount of Fe [mol %]	Conversion [%] ^[b]	Yield [%] ^[b]	Selectivity [%] ^[b,c]
1	Eco-Mn _{Ox3}	0.58*	3.35*	91	85	89
2	Eco-Mn _{Ox3}	0.31**	1.82**	59	41	80
3	Eco-Mn _{Ox3} /H ₂ O***	0.31**	1.82**	100	91	91
4	Montmorillonite K10	–	6.06	0	0	n.d. ^[d]
5	Eco-Mn _{LA1}	19.57	2.58	1	1	n.d. ^[d]

[a] Reaction conditions: styrene (0.25 mmol), H₂O₂ (30 wt%) (0.8 mmol), NaHCO₃ (0.2 M) (0.05 mmol), catalysts (*72 mg; **39 mg; *** 39 mg + 10 vol% H₂O), DMF (2 mL), 0 °C, 4 h. [b] Conversion and yield were determined by GC-MS after calibration, using biphenyl as an internal standard. [c] Ratio of yield to conversion as a percentage. [d] Not determined.

Table 11. Recycling and leaching studies of the supported Eco-Mn_{Ox3} catalyst for the epoxidation reaction of styrene over 4 successive reactions.^[a]

Recycling	Conversion [%] ^[b]	Yield [%] ^[b]	Selectivity [%] ^[b,c]	Post-run Mn content wt % ^[d]	Post-run Fe content wt % ^[d]
4 times	Stable 97–98	Stable 89–91	Stable 92–93	Less than 10% loss 0.087–0.079	Stable 0.64–0.66

[a] Reaction conditions: styrene (0.25 mmol), H₂O₂ (30 wt%) (0.8 mmol), NaHCO₃ (0.2 M) (0.05 mmol), recycled supported Eco-Mn_{Ox3} catalyst (39 mg), Mn 0.31 mol%, Fe 1.82 mol%, DMF/water 7:3 (2 mL), 0 °C, 4 h. [b] Conversion and yield were determined by GC-MS after calibration, using biphenyl as internal standard. [c] Ratio of yield to conversion as a percentage. [d] Determined by ICP-MS after EDTA extraction of a sample of supported Eco-Mn_{Ox3} catalyst following the reaction.

case of (*R*)-(+)-pulegone, where the C=C double bond is strongly deactivated by conjugation with a carbonyl group (Table 12, entry 6).

The method proved to be effective even on voluminous natural products, such as α -pinene, affording 75% yield of α -pinene epoxide, with complete selectivity (Table 12, entry 3). The Mn(II)-zeolite catalysts previously described in the literature were much less effective, indicating the advantage of the Eco-Mn_{Ox3} catalyst.^[82]

In agreement with the literature, the linalool epoxide rearranges as soon as it is formed,^[83] to give the hydroxypyrene with 63% yield (Table 12, entry 4).

Fair to good yields of epoxides with complex and bulky structures such as nopol (74%, Table 12, entry 9) and β -caryophyllene (42%, Table 12, entry 10) were obtained with excellent selectivity. However, the method proved to be ineffective with terminal aliphatic alkenes, such as *n*-octene, as already observed with other Mn(II) catalysts (Table 12, entry 11).^[82,84]

Indene, cyclooctene and cyclohexene epoxides were obtained in much higher yields than other catalysts based on Mn(II)-zeolite (Table 12, entries 12–14).^[82]

During the styrene epoxidation, a small amount of benzaldehyde was formed, suggesting that it might be possible to selectively obtain an aldehyde from an alkene by adjusting the reaction conditions. Indeed, by reproducing the optimal conditions of the epoxidation (4 h at 0 °C) and then heating the reaction medium to 80 °C styrene was quantitatively transformed into benzaldehyde (Table 13, entry 1).

The mechanism of the oxidative cleavage is firstly based on the formation of an epoxide, which is then open giving the corresponding diol. Then the diol undergoes an oxidative cleavage to form the corresponding aldehyde. This mechanism seems to be specific to Eco-Mn_{Ox3}. Indeed, a mixture of commercial salts MnCl₂·4H₂O/FeCl₃·6H₂O prepared in the same conditions as for the Eco-Mn_{Ox3} catalyst, leads to benzaldehyde with only 24% yield, accompanied by the corresponding 1,2-

diol, with 71% yield (Table 13, entry 2). This observation suggests that the limiting step is not the formation of the 1,2-diol but rather its subsequent cleavage.

Other alkenes were tested to determine the scope and limitations of the reaction. The presence of electron-withdrawing groups on the aromatic ring seemed to be unfavorable, since only 11% yield of aldehyde was obtained from 3-chlorostyrene (Table 14, entry 1). The corresponding epoxide, however, being formed with a yield of 68%, suggests that in this case the limiting step is the opening of the epoxide. The *trans*-anethole carrying both a methyl-enriched C=C double bond and a methoxy-group on the aromatic ring, gave a better yield of *p*-anisaldehyde (51% yield, Table 14, entry 2).

Reaction with cinnamyl acetate gave after heating, 53% of the desired product, benzaldehyde, was obtained and 19% of cinnamaldehyde was also observed (Table 14, entry 2).

In conclusion, Eco-Mn_{Ox3} catalyst allows a controlled access to aldehydes by oxidative cleavage of various alkenes. The developed process is therefore an interesting alternative not only to conventional epoxidation reagents, but also to oxidative cleavage process of styrene-derived alkenes, which generally involves the use of toxic and dangerous reagents.

3.3. Tandem sequential oxidation catalyzed by Eco-Mn_{LA} and Eco-Mn_{Ox} catalysts^[34]

Tandem sequential oxidation can be described as a multi-step process in which the substrate is transformed by two mechanistically distinct processes, one of which is an oxidation through the action of species present at the beginning of the reaction.^[85] Tandem processes reduce the number of operations, by allowing the preparation and *in-situ* reaction of reactive intermediates, thus avoiding their isolation and often preventing safety problems. Tandem processes are thus in line with the principles of green chemistry,^[86] and transition elements are frequently involved in tandem oxidation processes, as they often combine different chemical properties acting on different stages of the sequential reactions.^[87–90] Among these elements, manganese is the main topic of numerous publications devoted to tandem oxidation, mainly Mn(III)^[91–94] and Mn(IV).^[95–98] For instance, manganese has recently attracted wide interest for multicomponent reactions based on pincer-type manganese complexes.^[99–106]

Eco-Mn_{LA} and Eco-Mn_{Ox} catalysts possess a polymetallic composition which combines metal transition elements with Lewis or Brønsted acidity properties (Mn, Fe, Al) and oxidative properties (Mn, Fe). Eco-Mn_{LA} and Eco-Mn_{Ox} catalysts were studied in sequential tandem oxidation as a “Janus catalyst”, which is an eco-material with two different but concomitant catalytic properties.^[107,108] The ability to combine these two activities in a single material offers great benefits from a sustainable chemistry perspective, with reduced waste and process simplification.

Table 12. Substrate scope of the epoxidation catalyzed by supported Eco-Mn_{0x3} catalyst.^[a]

Entry	Substrate	Product	$ \begin{array}{c} \text{R}^1 \\ \diagup \\ \text{C}=\text{C} \\ \diagdown \\ \text{R}^2 \\ \text{R}^3 \\ \text{R}^4 \end{array} \xrightarrow[\text{DMF/H}_2\text{O (7:3), 0}^\circ\text{C}]{\text{EcoMnO}_{0x3} \text{ (Mn 0.31 mol\%, Fe 1.82 mol\%)}, \text{H}_2\text{O}_2, \text{NaHCO}_3} \begin{array}{c} \text{R}^1 \\ \diagup \\ \text{C}-\text{C} \\ \diagdown \\ \text{R}^2 \\ \text{R}^3 \\ \text{R}^4 \end{array} $			
			Solvent water content [vol%]	Conversion [%] ^[b]	Yield [%] ^[b]	Selectivity [%] ^[b,c]
1			0	100	99	99
2			5	50	43	86/14 (endocyclic/exocyclic epoxide)
3			0	75	75	100
4			0	65	63	97/3 (internal/terminal epoxide)
5			30	80	72	90/10 (mono/di epoxide)
6			30	49	27	55
7			15	81	78	96
8			5	74	50	68/16/16 (mono epoxide 2i/mono epoxide C ₅ /di epoxide)
9			30	77	74	96
10			0	46	42	91/9 (endocyclic/exocyclic epoxide)
11	n-Hex	n-Hex	0	0	0	n.d. ^[d]
12			30	100	98	98
13			0	60	55	92
14			0	95	89	94

[a] Reaction conditions: alkene (0.25 mmol), H₂O₂ (30 wt%) (0.8 mmol), NaHCO₃ (0.2 M) (0.05 mmol), supported Eco-Mn_{0x3} catalyst (39 mg, Mn 0.31 mol%, Fe 1.82 mol%), DMF/water (2 mL), 0 °C, 4 h. [b] Conversion and yield were determined by GC-MS after calibration, using biphenyl as internal standard. Synthesized products were identified by comparison of their spectroscopic data with those previously published. [c] Ratio of yield to conversion as a percentage. [d] Not determined.

Table 13. Oxidative cleavage of alkenes – comparison of Eco-Mn_{Ox3} catalyst with mixed salts.^[a]

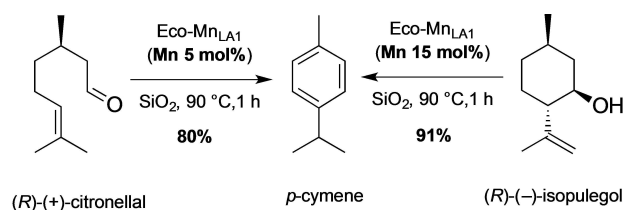
Entry	Catalyst	Conversion [%] ^[b]	Yield [%] ^[b]	Selectivity [%] ^[b,c]
1	Eco-Mn _{Ox3}	95	93	98
2	K10-supported MnCl ₂ ·4H ₂ O/ FeCl ₃ ·6H ₂ O	98	24 ^d	24

[a] Reaction conditions: alkene (0.25 mmol), H₂O₂ (30 wt%) (3.0 mmol), NaHCO₃ (0.2 M) (0.05 mmol), catalysts (39 mg, Mn 0.31 mol%, Fe 1.82 mol%), DMF/water 7:3 (2 mL), 0 °C, 4 h, then 80 °C, 24 h. [b] Conversion and yield were determined by GC-MS after calibration, using biphenyl as internal standard. Synthesized products were identified by comparison of their spectroscopic data with those previously published. [c] Ratio of yield to conversion as a percentage. [d] 1-phenyl-1,2-ethanediol was obtained as side-product with 71 % yield.

3.3.1. Tandem carbonyl-ene cyclisation and aromatization of citronellal to *p*-cymene catalyzed by Eco-Mn_{LA} catalyst

The conversion of natural products into aromatic derivatives is of great importance. The *p*-cymene is used as a building block in many industrial applications such as the production of pesticides, fungicides, flavor and fragrance components and pharmaceuticals.^[109,110] It can also be used as a ligand of hydrogenation catalysts such as [(η⁶-*p*-cymene) RuCl₂]₂.^[111] Currently, *p*-cymene is mainly produced by Friedel-Crafts alkylation of toluene with 2-propanol using acid catalysts such as AlCl₃ and HCl.^[112] This reaction is carried out at high temperatures (≥ 200 °C) and produces undesired isomers along with polyalkylation products. The yield of *p*-cymene generally does not exceed 50%.^[113]

In addition, the use of large quantities of acid catalysts and hazardous solvents causes many environmental and safety



Scheme 10. Conversion of (+)-citronellal or (–)-isopulegol into *p*-cymene catalyzed by Eco-Mn_{LA1}.

issues, such as the handling of reagents and solvents, waste disposal and corrosion problems.

Depending of the loading of Eco-Mn_{LA1} catalyst (5 mol% or 15 mol%), the synthesis of *p*-cymene can be performed from (+)-citronellal, a natural and abundant terpene, or from (–)-isopulegol under similar reaction conditions (Scheme 10).

Eco-Mn_{LA1} acted as a Janus catalyst in the transformation of (+)-citronellal into *p*-cymene, by promoting the carbonyl-ene reaction (Lewis acidity property) followed by the aromatization (oxidation). However, the catalysis of the last step was surprising, since Eco-Mn_{LA1} is supposed to lack any oxidizing properties. Indeed, Eco-Mn_{LA1} catalyst has Mn(II) species, which have no oxidative properties. The aromatization observed here might be due to the presence of oxidizing species, such as Mn(III) or Mn(IV), that might have been formed by oxidation of Mn(II) with O₂ present in the air. Previous studies have shown that the oxidation of Mn(II) to Mn(III) or Mn(IV) by atmospheric O₂ is a very slow process, but can be greatly accelerated with traces of Fe(III).^[114,115] As Eco-Mn_{LA} contains 0.90 wt% of Fe(III), the formation of such traces through this process is possible. Since Fe(III) is also an oxidizing agent, it is also possible that this species participates along with Mn(III) or Mn(IV) to the aromatization step.

Table 14. Substrate scope of oxidative cleavage catalyzed by Eco-Mn_{Ox3} catalyst.^[a]

Entry	Substrate	Product	Conversion [%] ^[b]	Yield [%] ^[b]	Selectivity [%] ^[b,c]
1			79	11 ^[d]	14
2			72	51	71
3			72	53 ^[e]	74

[a] Reaction conditions: alkene (0.25 mmol), H₂O₂ (30 wt%) (3.0 mmol), NaHCO₃ (0.2 M) (0.05 mmol), catalysts (39 mg, Mn 0.31 mol%, Fe 1.82 mol%), DMF/water 7:3 (2 mL), 0 °C, 4 h, then 80 °C, 24 h. [b] Conversion and yield were determined by GC-MS after calibration, using biphenyl as internal standard. Synthesized products were identified by comparison of their spectroscopic data with those previously published. [c] Ratio of yield to conversion as a percentage. [d] 3-chlorostyrene epoxide was formed with 68% yield. [e] cinnamaldehyde was obtained as side-product with 19% yield.

3.3.2. One pot synthesis of substituted pyridines catalyzed by Eco-Mn_{LA} catalyst

The couple dihydropyridine/pyridine (or pyridinium) is the synthetic analog of NADPH/NADP⁺, a cofactor involved in natural redox systems. The couple dihydropyridine/pyridine is a useful combination to conduct traditional chemical reductions or oxidations in many examples.^[116] The mechanism is based on a hydride transfer from dihydropyridine towards an electrophilic center (carbonyl compounds, imines, unsaturated carbonyl compounds), in which the driving force is the developing aromaticity of the pyridine cycle.^[116]

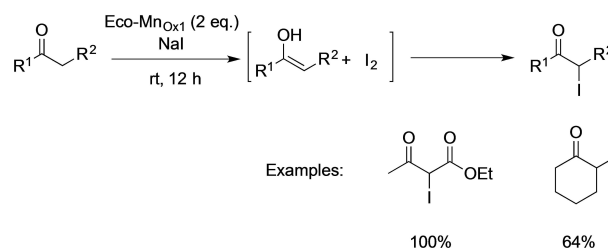
The preparation of 1,4-dihydropyridine is based on Hantzsch reaction between aldehydes, β -keto esters, and amines. The synthesis of pyridines can be performed by aromatization of dihydropyridines with various reagents such as HNO₃,^[117] (NH₄)₂Ce(NO₃)₆,^[118] Cu(NO₃)₂,^[119] Bi(NO₃)₃·5H₂O,^[120] Mn(OAc)₃,^[121] Zr(NO₃)₄,^[122] Fe(NO₃)₃,^[123] PCC,^[124] Pd/C,^[125] I₂/MeOH,^[126] *o*-iodoxybenzoic acid (IBX),^[127] SeO₂,^[128] KBrO₃/SnCl₄·5H₂O,^[129] KMnO₄,^[130] MnO₂ under microwave irradiation or sonication^[119] and DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone).^[131] Despite these numerous works, the development of effective and green methods are still required.

In this context, Eco-Mn_{LA1} catalyst has proved to be an elegant solution in the direct synthesis of pyridines, obtained by *in-situ* oxidation of 1,4-dihydropyridines (DHP) resulting from the Hantzsch reaction. This reaction constitutes a second example of tandem sequential reaction.

The catalytic potential of Eco-Mn_{LA1} was studied under microwave irradiation after dispersion of the catalyst and reagents in silica gel. Surprisingly, none of the 1,4-dihydropyridines was observed, only the corresponding pyridine was obtained. Interestingly, the reaction is compatible with aromatic aldehydes as well as enolizable aldehydes, as phenyl acetaldehyde (69–96%) (Scheme 11).

3.3.3. Oxidative iodination of ketones catalyzed by Eco-Mn_{Ox1} catalyst

The α -iodinated ketones are widely used and studied. Indeed, they have a high reactivity and can be used as intermediates for the synthesis of useful high added-value compounds, including pharmacologically active heterocycles.^[132] The synthesis of α -iodoketones frequently involves the formation of electrophilic derivatives of iodine,^[133] using I₂ in combination with various



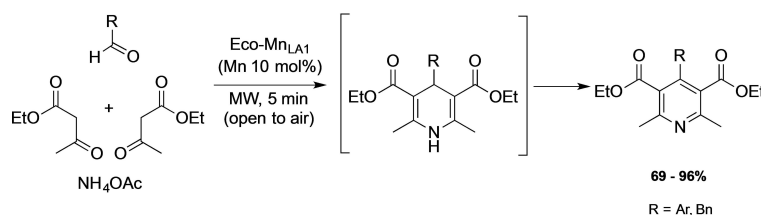
Scheme 12. Direct oxidative iodination of ketones with NaI/Eco-Mn_{Ox1}. Reaction conditions: ketone (1 mmol), Eco-Mn_{Ox1} (2 mmol Mn), NaI (1 mmol) in CH₃OH (5 mL) at room temperature for 12 h.

oxidizing reagents, such as SeO₂,^[134] Ce(IV) ammonium nitrate^[135] or *m*-iodosobenzoic acid.^[136] Despite their efficiency, these methods use toxic or unstable oxidizing reagents that are incompatible with the requirements of the REACH regulation. Moreover, since I₂ is a rather aggressive compound, its handling is problematic, especially on a large scale. For these reasons, various groups have proposed new methodologies involving the *in-situ* formation of electrophilic iodine by oxidation of safe iodide species such as NaI, KI or NH₄I. Selected examples of this strategy include the use of NaI/H₂O₂/H₂SO₄,^[137] KI/air/H₂SO₄/NaNO₂^[138] or NH₄I/Oxone[®].^[139] Although these methods represent significant improvements, they still use corrosive acids (H₂SO₄) or highly toxic compounds (NaNO₂).

The potential of Eco-Mn_{Ox1} has been studied in oxidative iodination of ketones, as an alternative and safe oxidative reagent, with NaI as the source of iodine (Scheme 12).

Thanks to its Lewis and Brønsted character, Eco-Mn_{Ox1} is able to promote the enolization of the ketones. At the same time, the oxidizing properties of Eco-Mn_{Ox1} allowed the *in-situ* formation of iodine, immediately consumed by reaction with the enolized ketone and thus forming the α -iodoketone.

In the case of the β -dicarbonyl compounds, 2 equivalents of Eco-Mn_{Ox1} at room temperature leads to a quantitative reaction after 12 h. Under the same conditions, cyclohexanone was directly iodinated to give 2-iodocyclohexanone with a yield of 64%, thus confirming the activity of the system in the case of less easily enolizable ketones. Eco-Mn_{Ox1} is therefore a valuable ecological alternative to more harmful or unstable oxidizing reagents, avoiding the use of strong acids and toxic species.



Scheme 11. Tandem DHP synthesis-oxidation into pyridine with Eco-Mn_{LA1}. Reaction conditions: Eco-Mn_{LA1} (0.05 mmol Mn), silica gel (1 g), aldehyde (0.5 mmol), ethyl acetoacetate (1.0 mmol), ammonium acetate (0.75 mmol), MW irradiation 5 × 1 min at 600 W.

4. Summary and outlook

Mn-accumulating plants of the *Grevillea* genus, that are used for the rehabilitation of metal contaminated mining sites, produce a biomass enriched in Mn and valuable for synthetic chemical applications. Using simple transformation procedures, the plant-based biomass led to the first bio-sourced Mn-catalysts, Eco-Mn catalysts. The ICP-MS, XRD and XAS analyses revealed that the Eco-Mn catalysts contained original polymeric complexes, which are linked to their unique reactivity. Eco-Mn_{LA} catalysts showed a marked Lewis and Brønsted acidity, which makes them very competitive to other classical catalysts, for the preparation of enol ethers and the cyclisation of (+)-citronellal carbonyl-ene to isopulegol. Eco-Mn_{LA} catalysts were also used in reductive catalysis, for reductive aminations of ketones when associated with the Hantzsch ester.

Three types of eco-catalysts with oxidative properties, Eco-Mn_{OX}, were prepared using Eco-Mn_{LA1} as a starting material. Eco-Mn_{OX} catalysts were used as green and efficient oxidizing reagents for the controlled oxidation of allyl and benzyl alcohols to aldehydes as well as for the oxidative cleavage of diols and a functionalized polyol with very good yields.

Both Eco-Mn_{LA} and Eco-Mn_{OX} also behaved as Janus-type catalysts by promoting sequential tandem oxidation reactions, thanks to their Lewis acid character and oxidative properties.

The new concept of Ecocatalysis allowed the preparation of a wide range of efficient and ecological Eco-Mn catalysts with flexible reactivity, while respecting the principles of Green Chemistry. Eco-Mn allowed to revisit two major mechanisms of organic synthesis and to develop green substitution reagents for oxidants prohibited by REACH regulation. Ecocatalysts pave the way for sustainable chemistry able to combine efficiency, speed, Nature-origin and eco-responsibility.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Green chemistry · Ecocatalysis · Lewis acid catalysis · Sustainable oxidation · Sequential tandem reaction

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