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Lewis acid catalysis and Green oxidations: sequential tandem oxidation processes induced by Mn-hyperaccumulating plants

Vincent Escande · Brice-Loïc Renard · Claude Grison

Abstract Among the phytotechnologies used for the reclamation of degraded mining sites, phytoextraction aims to diminish the concentration of polluting elements in contaminated soils. However, the biomass resulting from the phytoextraction processes (highly enriched in polluting elements) is too often considered as a problematic waste. The manganese-enriched biomass derived from native Mn-hyperaccumulating plants of New Caledonia was presented here as a valuable source of metallic elements of high interest in chemical catalysis. The preparation of the catalyst Eco-Mn_1 and reagent Eco-Mn_2 derived from *Grevillea exul exul* and *Grevillea exul rubiginosa* was investigated. Their unusual polymetallic compositions allowed to explore new reactivity of low oxidative state of manganese—Mn(II) for Eco-Mn_1 and Mn(IV) for Eco-Mn_2. Eco-Mn_1 was used as a Lewis acid to catalyze the acetalization/elimination of aldehydes into enol ethers with high yields; a new green and stereoselective synthesis of (−)-isopulegol via the carbonyl-ene cyclization of (+)-citronellal was also performed with Eco-Mn_1. Eco-Mn_2 was used as a mild oxidative reagent and controlled the oxidation of aliphatic alcohols into aldehydes with quantitative yields. Oxidative cleavage was interestingly noticed when Eco-Mn_2 was used in the presence of a polyol. Eco-Mn_2 allowed direct oxidative iodination of ketones without using iodine, which is strongly discouraged by new environmental legislations. Finally, the combination of the properties in the Eco-Mn catalysts and reagents gave them an unprecedented potential to perform sequential tandem oxidation processes through new green syntheses of *p*-cymene from (−)-isopulegol and (+)-citronellal; and a new green synthesis of functionalized pyridines by in situ oxidation of 1,4-dihydropyridines.

Keywords Phytoextraction · Green chemistry · Tandem oxidation · Lewis acid catalysis · Manganese · Ecocatalysis · Metal-hyperaccumulating plants

Introduction

The chemistry of manganese is largely known for the high oxidation state of Mn that is Mn(VII), and thus for the oxidative abilities of $KMnO_4$ (Lee et al. 2001). Until recently, the lower oxidation states, Mn(IV), Mn(III), and Mn(II) were less used in organic synthesis. MnO_2 has led to more restricted outlet in synthesis than $KMnO_4$, because it needs to be prepared under active form for displaying its oxidizing properties. It has been found to be a mild oxidizing agent with a low reactivity (Cahiez et al. 2001a). Application of Mn(III) in organic chemistry has recently emerged, especially in radical reactions (Snider et al. 2001). As Mn(II) is considered as a weak Lewis acid (Cahiez et al. 2001b), its use in catalysis remains limited.

Besides, the development of "Ecocatalysis", which has been initiated by our group (Escande et al. 2014a; Grison and Escande 2013a, b; Grison et al. 2013; Grison and Escarré 2011; Losfeld et al. 2012), has already shown unexpected outstanding reactivity of Lewis acids in ecocatalysts derived from hyperaccumulating plants. For instance, commercial $NiCl_2$ is considered as a weak Lewis acid, but Eco-Ni has shown very strong Lewis acid properties and has allowed the catalysis of unprecedented green reductions. The new reactivity of ecocatalysts has been explained by the synergic effect of other cationic metals, hyperaccumulated by the plants. Therefore, new applications of low oxidation states of Mn in organic

V. Escande · B.-L. Renard · C. Grison (✉)
Laboratoire de Chimie bio inspirée et Innovations écologiques,
FRE 3673 ChimEco CNRS-UM2, Stratoz, Cap Alpha-Avenue
de l'Europe, Clapiers, 34830 Montpellier, France
e-mail: claude.grison@cnrs.fr

chemistry were explored here through an alternative resource of Mn derived from Mn-hyperaccumulating plants.

In the present work, Mn-hyperaccumulating plants (>1 % of Mn (*w*/*w*) in dry leaf tissue (Baker and Brooks 1989; van der Ent et al. 2013)) were cultivated on New Caledonian sites, which had been degraded by the mining industry. Among the Mn-hyperaccumulating species present in New Caledonia (Brooks et al. 1981; Fernando et al. 2008; Jaffre 1977, 1979), *Grevillea exul* (Proteaceae) was a pioneering plant in revegetation trials, capable of growing rapidly and able to hyperaccumulate the highest concentration of Mn in shoots. *G. exul* were thus cultivated on such polluted sites in a phytoextraction process to provide a rich source of manganese and others transition metals. The conversion of *G. exul* shoots into ecocatalysts produced Eco-Mn_1 and Eco-Mn_2, composed of Mn(II) and Mn(IV), respectively. Their detailed compositions were investigated by inductively coupled plasma mass spectrometry (ICP-MS) and X-ray diffraction (XRD) analyses before use in organic synthesis. The unusual polymetallic species present in Eco-Mn_1 and in Eco-Mn_2, showed respectively unprecedented strong Lewis acid properties of Mn(II) and a controlled oxidative reactivity of Mn(IV) strengthened by the presence of Lewis acids in the plant-based extract. The combination of the two factors allowed the Eco-Mn to promote sequential tandem reactions of acid catalysis/oxidation.

Materials and methods

Chemicals

Reagents and solvents were purchased from Sigma-Aldrich and were used without further purification.

Preparation of Eco-Mn

Preparation of Eco-Mn_1

Two subspecies of *G. exul* are present in New Caledonia: *G. exul exul* and *G. exul rubiginosa* (Jaffre 1979), being both capable of hyperaccumulating manganese. In order to compare the possible differences in manganese accumulation, two Eco-Mn_1 have been prepared, derived from the two subspecies.

Leaves of *G. exul* (same treatment for ssp. *exul* and *rubiginosa*) were harvested before flowering in the Southern Province of the subtropical Pacific island of New Caledonia, in homogeneous vegetal populations. *G. exul exul* was collected in Camp des sapins mining site, near Thio; *G. exul rubiginosa* was collected at Col de Mouriange, near Le Mont-Dore. The leaves were air-dried and grounded. The obtained solid (50 g) was calcined to 400 °C for 5 h and the resulting powder (1.5 g) was added to 20 mL of a diluted solution of HCl (1 M). The solution was stirred for 2 h at 60 °C. During heating, the color of the mixture evolved from black to dark green. The reaction mixture was then filtered on a pad of celite. The resulting dark-green solution, composed of different metal chlorides, was concentrated under vacuum, yielding Eco-Mn_1 as a pale yellow powder (2.09 g from *G. exul exul*, 2.25 g from *G. exul rubiginosa*). The resulting Eco-Mn_1 catalyst was stored in a desiccator under vacuum. Purification steps are not mandatory in our process.

Preparation of Eco-Mn_2

The preparation of Eco-Mn_2 relied on the oxidation of Mn(II) from Eco-Mn_1 into Mn(IV), by dioxygen from air at atmospheric pressure, in slightly alkaline medium. Following the Pourbaix diagram of manganese (Fig. 1), the standard potential of Mn(IV)/Mn(II) decreases when pH increases. At pH 8, Mn(II) formed a precipitate under the form of Mn(II) hydroxide ($Mn(OH)_2$). The standard potential of O_2/H_2O was higher than the standard potential of ($Mn(OH)_2$) at pH 8. The oxidation of Mn(II) by dioxygen was then possible and led to Mn_3O_4 and Mn_2O_3. The oxidation of Mn(II) into Mn_2O_3 (Mn(III)) and Mn_3O_4 (Mn(II,III)) was rapidly visible, as the solution turns from light yellow to black in a few hours (Fig. 2). As Fe(III) was also present in the starting Eco-Mn_1 catalyst, it was equally precipitated into Fe_2O_3, following its Pourbaix diagram (Fig. 3).

Mn_2O_3 (Mn(III)) and Mn_3O_4 (Mn(II,III)) were eliminated by disproportionation into Mn^{2+} (Mn(II)) and MnO_2 (Mn(IV)) by acidification at pH 3, according to the following equations (Artamonova et al. 2013):

$$Mn_3O_4 + 2H^+ \rightarrow Mn^{2+} + Mn_2O_3 + H_2O \tag{1}$$

$$Mn_2O_3 + 2H^+ \rightarrow Mn^{2+} + MnO_2 + H_2O \tag{2}$$

After acidification at pH 3, Fe_2O_3 was equally transformed into soluble Fe^{3+} ions. Acidification was performed with diluted hydrochloric acid, Mn(II) and Fe(III) were therefore present as hydrated chlorides in the solution. The final mixture was composed of MnO_2 in combination with Mn(II) and Fe(III) chlorides, which can act as Lewis acids as observed in Eco-Mn_1.

In a typical procedure, 50 mg of Eco-Mn_1 (0.061 mmol of Mn) were introduced in a 25-mL flask. After addition of water (10 mL), a light yellow solution was obtained. The pH of the solution was adjusted to 8 by addition of a few drops of aqueous solution of sodium hydroxide (0.01 M). A brownish-orange precipitate was immediately formed. The flask was open to air and the solution was stirred at room temperature. After 2 h, the color of the solution became dark brown, then black. No evolution of color was observed after 5 h. After 7 h,

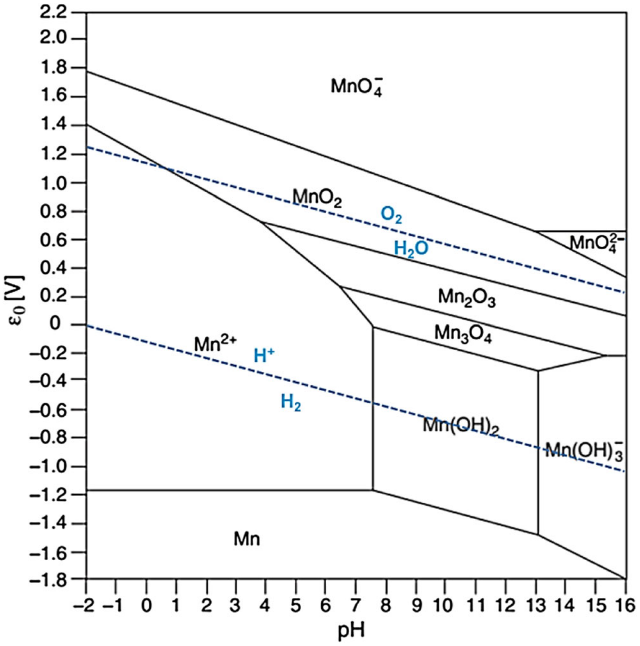


Fig. 1 Pourbaix diagram of manganese. Adapted from Fränzle (2010)

the black solid was collected by centrifugation then washed with water (3×15 mL) in order to eliminate the excess of sodium hydroxide. After addition of water (10 mL), the pH of the solution was then adjusted to pH 3 by addition of a few drops of diluted hydrochloric acid (0.1 M). After evaporation of the liquid phase under reduced pressure, a brilliant black powder was collected, dried, and stored in a vacuum desiccator over P_2O_5, yielding 5.5 mg of Eco-Mn_2.

Characterization of Eco-Mn_1

ICP-MS was used to determine the composition of Eco-Mn_1 and Eco-Mn_2.

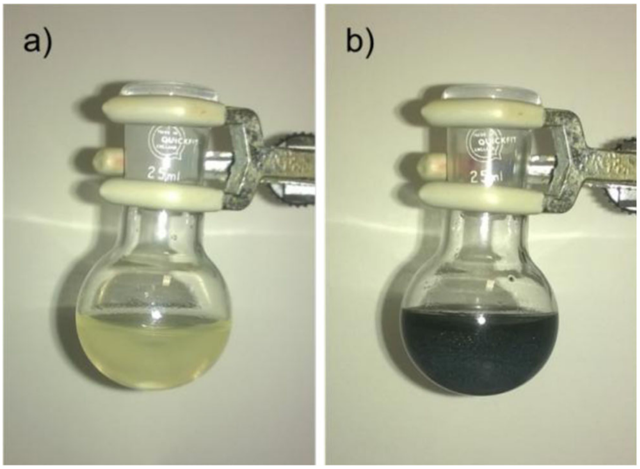


Fig. 2 Oxidation of Mn(II) from Eco-Mn_1 into Mn_2O_3 (Mn(III)) and Mn_3O_4 (Mn(II,III)) by air: **a** before basification, **b** 7 h of agitation in contact with air at pH 8

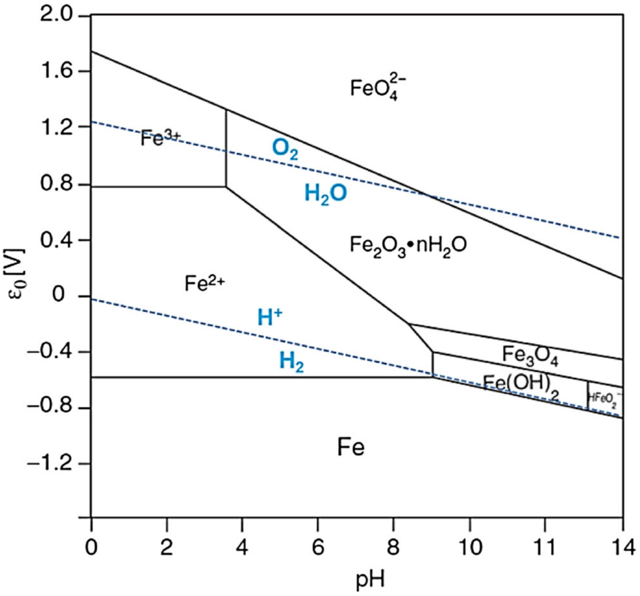


Fig. 3 Pourbaix diagram of iron. Adapted from Fränzle (2010)

ICP-MS analyses were performed using the metal analysis of total dissolved solutes in water. The samples were acidified with nitric acid 2.5 % and stirred for 30 min. The digestates were diluted to 0.005 g.L^{-1}. Three blanks were recorded for each step of the digestion and dilution procedure on a HR-ICP-MS Thermo Scientific Element XR. Three analyses were performed for each sample in order to determine the standard deviation of the measurement.

XRD data measurements on the samples dried at 110 °C for 2 h were performed by using a BRUKER diffractometer (D8 advance, with a Cu Kα radiation λ=1.54086°A) equipped with a Lynxeyes detector.

FT-IR measurements were carried out using pyridine as probe molecule. A PerkinElmer Spectrum 100 FT-IR spectrometer was used for recording spectra. Excess gaseous pyridine was adsorbed on the samples, then the samples were degassed for 15 min at 25 °C (10^{-3} Pa) and a first spectrum was recorded. The samples were then degassed for 15 min at 150 °C (10^{-3} Pa) to eliminate the physisorbed pyridine and a second spectrum was recorded.

Syntheses catalyzed by Eco-Mn_1

Synthesis of alkyl enol ethers from aldehydes

In a typical procedure, to a solution of aldehyde (1.0 mmol) in anhydrous ethanol (3.0 mL) was added Eco-Mn_1 (82 mg, amount corresponding to 0.10 mmol of Mn). The suspension was refluxed for 5 h (reaction monitored by GC-MS analysis), then without elimination of the catalyst, the mixture was slowly distilled under reduced pressure (40 mmHg) affording the corresponding ethyl enol ether. Spectroscopic data (^{1}H

NMR, IR) were in accordance with the data previously published (Barbot and Miginiac 1979).

Synthesis of isopulegol via the carbonyl-ene cyclization of (+)-citronellal

To a suspension of Eco-Mn_1 (16.4 mg, amount corresponding to 0.020 mmol of Mn) in 10 mL of dichloromethane was added 180.4 μL of (+)-citronellal (1.0 mmol). After stirring for 0.5 h under reflux, the reaction mixture was filtered and washed with a saturated aqueous solution of $NaHCO_3$. The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. A yield of 95 % and 90 % of (−)-isopulegol stereoselectivity were estimated by GC-MS analysis. ^{1}H NMR and IR data were in accordance with those previously reported (Imachi et al. 2007).

*Synthesis of **p**-cymene from (+)-citronellal*

To 5 mg of Eco-Mn_1 (amount corresponding to 0.006 mmol of Mn) co-ground with 100 mg of silica gel, was added (+)-citronellal (21.8 μL, 0.12 mmol). After stirring for 1 h at 90 °C, the reaction mixture was washed with dichloromethane and filtered through celite. The solution was concentrated under reduced pressure. A yield of 80 % of *p*-cymene with 5 % of (−)-isopulegol were estimated by GC-MS. *p*-Cymene identification was performed by comparing retention times and MS spectra with a commercial sample.

*Synthesis of **p**-cymene from (−)-isopulegol*

To 15 mg of Eco-Mn_1 (amount corresponding to 0.018 mmol of Mn) co-ground with 100 mg of silica gel, was added (−)-isopulegol (20 μL, 0.12 mmol). After stirring for 1 h at 90 °C, the reaction mixture was washed with dichloromethane and filtered through celite. The solution was concentrated under reduced pressure. A yield of 91 % of *p*-cymene was estimated by GC-MS. *p*-Cymene identification was performed by comparing retention times and MS spectra with a commercial sample.

Synthesis of diethyl 2,6-dimethyl-4-phenyl-3,5-pyridinedicarboxylate

In a typical procedure, to a co-ground mixture of silica gel (1 g) and Eco-Mn_1 (42 mg, amount corresponding to 0.05 mmol of Mn) were added benzaldehyde (51 μL, 0.5 mmol), ethyl acetoacetate (126 μL, 1.0 mmol), and ammonium acetate (58 mg, 0.75 mmol). After homogenization of the mixture with spatula, the resulting white powder was poured into a glass vial (4 mL) open to air then irradiated in a domestic microwave oven (DeLonghi, Perfecto Easy) at 600 W for 5×1 min (with intervals of 1 min for cooling at room temperature). Progress of the reaction was followed by GC-MS analysis. The solid turned quickly to yellow. After washing of the solid with dichloromethane then filtration, the organic layer was washed with saturated $NaHCO_3$ solution, then with brine, dried over Na_2SO_4 then concentrated under reduced pressure. The crude product was purified by recrystallization in an ethyl acetate-ether mixture. A yield of 91 % of diethyl 2,6-dimethyl-4-phenyl-3,5-pyridinedicarboxylate **15a** was obtained. ^{1}H NMR, IR, and MS data were in accordance with the data previously published (Kumar and Kumar 2010).

Syntheses catalyzed by Eco-Mn_2

Controlled oxidation of alcohols into aldehydes

In a typical procedure, to a suspension of Eco-Mn_2 (4.43 g, amount corresponding to 38.9 mmol of Mn) in 20 mL of EtOAc was added 4-hydroxy-3-methoxybenzyl alcohol **4b** (1.54 g, 10 mmol) under inert atmosphere. The reaction was monitored by GC-MS. After stirring for 3 h under reflux, the reaction mixture was filtered and the solid was washed with EtOAc. The solution was concentrated under reduced pressure to give vanillin **5b** with quantitative yield (estimated by GC-MS). Vanillin was identified by comparing retention times, IR, and MS spectra with a commercial sample.

Oxidative cleavage of polyol

To a suspension of Eco-Mn_2 (684 mg, amount corresponding to 6.0 mmol of Mn) in 20 mL of acetonitrile was added ethyl 2-methyl-5-((1*S*,2*R*,3*R*)-1,2,3,4-tetrahydroxybutyl)furan-3-carboxylate **6** (274 mg, 1.0 mmol). After stirring for 5 h at room temperature (the reaction was monitored by IR), the reaction mixture was filtered through celite and the solid was washed with dichloromethane. The solution was concentrated under reduced pressure, affording ethyl 5-formyl-2-methylfuran-3-carboxylate **7** as a white solid, after recrystallization in dichloromethane, in quantitative yield. ^{1}H NMR and IR data were in accordance with those previously reported (Moreno-Vargas et al. 2001).

Direct oxidative iodination of ketones

To a solution of cyclohexanone (103.6 μL, 1.0 mmol) in methanol (5 mL) was added sodium iodide (149.9 mg, 1.0 mmol) and Eco-Mn_2 (228 mg, amount corresponding to 2.0 mmol of Mn). After stirring at room temperature for 12 h (reaction monitored by GC-MS), the mixture was filtered on a pad of celite then washed with a solution of sodium thiosulfate (2 M), dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The corresponding 2-iodocyclohexanone was obtained with 64 % yield. ^{1}H NMR and IR data were in accordance with the data previously published (Aizpurua et al. 1985).

Purification and analysis of products

Flash column chromatography was performed using Chromagel Carlo Erba Reactifs SDS silica 60 A CC 35–70 µm. Reactions were monitored using Merck Kieselgel 60 F254 aluminum. TLC's were visualized by UV fluorescence (254 nm) then by immersion in one of the following dyeing reagents: $KMnO_4$, vanillin, ninhydrin, phosphomolybdic acid solution, or phosphotungstic acid solution.

NMR spectra were recorded on a Brüker Avance 300 spectrometer at room temperature, ^{1}H frequency is at 300 MHz, ^{13}C frequency is at 75 MHz. IR spectra were recorded on a PerkinElmer Spectrum 100 FT-IR spectrometer, in ATR mode. GC-MS analyses were performed on a Shimadzu QP2010SE apparatus, equipped with a 30 m× 0.25 mm×0.25 µm ZB-5MSi Guardian column (Phenomenex®) with hydrogen as carrier gas.

Results and discussion

Starting from shoots of *G. exul* used in phytoextraction processes on degraded mining sites of New Caledonia, two types of Eco-Mn have been conceived, with different chemical compositions and properties.

Eco-Mn_1: a bivalent Lewis/Brønsted acid catalyst

Eco-Mn_1 has been obtained by thermic treatment of leaves of *G. exul rubiginosa*, then acid treatment of the resulting powder, as a polymetallic extract enriched in Mn(II), with Lewis and Brønsted acid properties.

There are very few mentions of Mn(II) as Lewis acid catalyst in the literature (Horike et al. 2008; Roy et al. 2010). Mn(II) salts are usually described as weak Lewis acids, which may explain their almost absence in the field of Lewis acid catalysis (Cahiez et al. 2001b). Herein, we describe the preparation, characterization, and use of Eco-Mn_1 as a novel bivalent Lewis and Brønsted acid catalyst, derived from Mn-hyperaccumulating plants. Unlike classical Mn(II) salts, Eco-Mn_1 proved to be an efficient acid catalyst due to its original polymetallic composition.

Characterization of Eco-Mn_1

ICP-MS analysis of Eco-Mn_1 ICP-MS analyses of Eco-Mn_1 were performed after dilution of the solid in an aqueous solution of 2.5 % nitric acid (Table 1).

The analysis showed that Mn was the major transition metal in the two ecocatalysts. But ecocatalyst derived from *G. exul rubiginosa* was more concentrated in Mn (6.72 wt%) than ecocatalyst derived from *G. exul exul* (5.90 wt%). This observation was consistent with data previously published (Jaffre 1979). A small amount of Ni was observed in the two ecocatalysts. Fe was the second most abundant transition metal in both ecocatalysts, with contents of 1.81 wt% in Eco-Mn_1 from *G. exul exul* and 0.90 wt% in Eco-Mn_1 from *G. exul rubiginosa*. The quantities of Mg, Ca, and Al were similar between the two ecocatalysts. Because of the higher concentration of Mn in *G. exul rubiginosa*, we chose to focus on this subspecies to produce Eco-Mn_1. The reproducibility of the composition of similar ecocatalysts was studied in a previous article (Escande et al. 2014b), which showed that the levels of transition elements are only slightly variable between samples derived from different plants. The Eco-Mn_1 was prepared from several batches of *G. exul rubiginosa* in order to homogenize the content of the transition elements and minimize possible variations in the composition.

XRD analysis of Eco-Mn_1 XRD analysis has been performed in order to investigate the structure of the Eco-Mn_1 catalyst (Fig. 4 and Table 2). Two polymetallic chlorides were detected: $CaMg_2Cl_6(H_2O)_{12}$ and $KMnCl_3$, which was a masked form of $MnCl_2$. Manganese was thus present in Eco-Mn_1 under the oxidation state Mn(II).

XRD did not reveal the presence of molecules containing Fe or Al, which were detected by the elemental analysis. This was probably due to the non-crystalline nature of these species within the Eco-Mn_1 catalyst. As regards the oxidation state of iron in Eco-Mn_1, a colorimetric test with ammonium thiocyanate demonstrated that iron was present under the oxidation state Fe(III) in the catalyst (Feigl and Anger 1972).

Infrared characterization of the Lewis and Brønsted acidities of Eco-Mn_1 by pyridine adsorption The Lewis acid properties of the Eco-Mn_1 were investigated by infrared characterization after pyridine adsorption. Pyridine is widely used for the determination of Lewis acidity of solid acids, by monitoring the bands in the range of 1400–1650 cm^{-1} arising from its ring vibration modes (Parry 1963; Zaki et al. 2001). Infrared spectra of pyridine adsorbed on Eco-Mn_1 were acquired at 25 °C and 150 °C in order to distinguish frequencies of physisorbed pyridine from frequencies of pyridine coordinated to Lewis acid sites (Fig. 5).

In Fig. 5, a band at 1443 cm^{-1} was observed at 25 °C and shifted to 1446 cm^{-1} after outgassing at 150 °C. This shift was attributed to the disappearance of physisorbed, weakly bonded pyridine. After outgassing at 150 °C, only strongly bonded pyridine persisted, by coordination to Lewis acid sites (Parry 1963). A similar phenomenon was observed in the range 1570–1640 cm^{-1}. Several frequencies, characteristic of physisorbed pyridine, present at 1573, 1592, and 1600 cm^{-1} at 25 °C, disappeared after outgassing at 150 °C. In the same range, higher frequencies were recorded after outgassing at elevated temperature (1604 and 1611 cm^{-1}). The presence of bands in

Table 1 ICP-MS analysis of Eco-Mn_1 from *Grevillea exul exul* and *Grevillea exul rubiginosa*

Ecocatalyst	Mg wt% (±sd)	Ca wt% (±sd)	Al wt% (±sd)	Mn wt% (±sd)	Fe wt% (±sd)	Ni wt% (±sd)
Catalyst derived from *Grevillea exul exul*	4.68 (±0.10)	10.91 (±0.20)	0.39 (±0.018)	5.90 (±0.044)	1.81 (±0.0090)	0.12 (±0.00046)
Catalyst derived from *Grevillea exul rubiginosa*	5.26 (±0.086)	10.44 (±0.17)	0.24 (±0.015)	6.72 (±0.037)	0.90 (±0.0075)	0.040 (±0.00039)

this range, in spite of heating at high temperature, indicated the presence of strongly bonded pyridine coordinated to Lewis acid sites. It showed the Lewis acidity of Eco-Mn_1.

Moreover, the occurrence of the bands at different frequencies in this range may account for the involvement of different types of Lewis acid sites (Zaki et al. 2001). The hypothesis was supported by the previous X-ray data (Table 2), highlighting the presence of different Lewis acids in Eco-Mn_1.

In the middle part of the spectra, a band near 1530 cm^{-1} was weak at 25 °C but became very intense after degassing at 150 °C. This band has been described as characteristic of the frequency ν_{19b} of the pyridinium ion formed by protonation of pyridine by Brønsted acid (Zaki et al. 2001). The intensity increasing while degassing at 150 °C was connected to the influence of heating on the kinetics of the pyridine protonation. Eco-Mn_1 comprised thus a Brønsted acid character in addition to a Lewis acid character. This Brønsted acidity probably resulted from the hydrolysis of metal chlorides present in Eco-Mn_1 (such as Mn or Fe chlorides) because of the presence of hydrated salts (such as $CaMg_2Cl_6(H_2O)_{12}$) in the catalyst, as highlighted by XRD experiments (see above). A test on wet pH indicator paper confirmed the acidity. A pH measurement of a clear solution of Eco-Mn_1 in water (12 mg in 20 mL) indicated a pH of 4.5. Such Lewis/Brønsted acid properties suggested that Eco-Mn_1 combined novel interesting catalytic properties for organic synthesis. The catalytic potential of Eco-Mn_1 was thus explored in a set of Lewis/Brønsted acid-catalyzed reactions.

Lewis/Brønsted acid catalysis with Eco-Mn_1

Formation of alkyl enol ethers by acetalization/dealcoholation from aldehydes Alkyl enols ethers are of great synthetic interest. They are very reactive toward electrophilic moieties, particularly carbonyl groups and are used for the formation of C–C bonds in organic synthesis. Compared to their metal

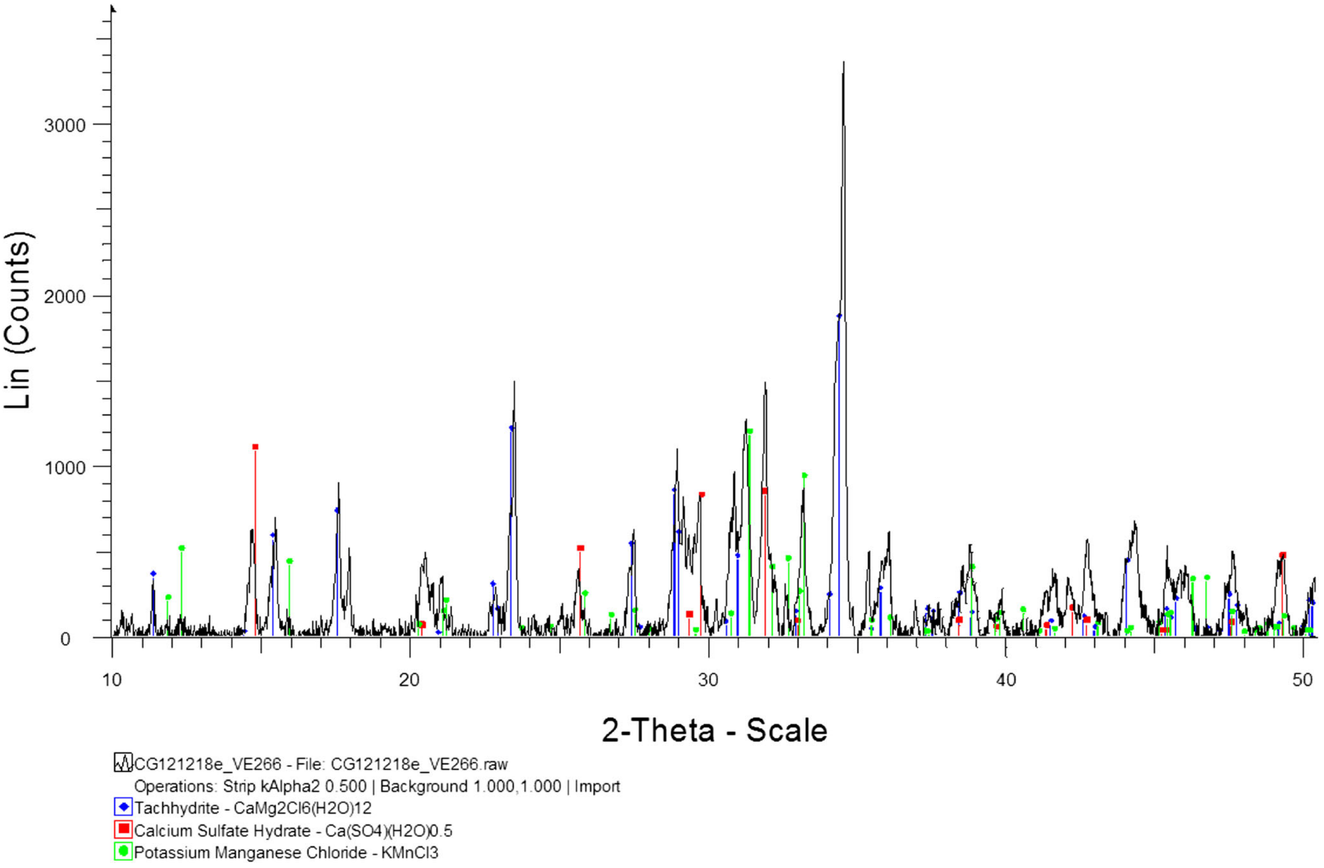


Fig. 4 Characterization of Eco-Mn_1 by XRD

Table 2 Crystalline species present in Eco-Mn_1 catalyst and detected by XRD

Mineral	Formula (simplified)
Calcium magnesium chloride hydrate	$CaMg_2Cl_6(H_2O)_{12}$
Calcium sulfate hydrate	$CaSO_4(H_2O)_{0.5}$
Potassium manganese chloride	$KMnCl_3$

enolate equivalents, 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 (Chavez and Jacobsen 2003; Gademann et al. 2002). An abundant literature is available concerning the preparation of alkyl enol ethers and their synthetic applications (Chan 1991; Gassman et al. 1993; Huisgen 1977). Notable examples of compounds synthesized with alkyl enol ethers include β-carotene, retinal (vitamin A aldehyde) and its derivatives (Isler et al. 1956; Makin 1976), pyrrolidine alkaloids (Shono et al. 1981), iridoid natural products (Chavez and Jacobsen 2003) and tetrahydroquinoline derivatives (Akiyama et al. 2006), with potential biological activity (Fig. 6).

Classical methods of preparation of alkyl enol ethers involve the use of harsh conditions, such as strong bases (e.g. *n*-butyllithium (*n*-BuLi), lithium diisopropylamide (LDA), sodium hydride), in organic solvents associated with environmental damages (e.g. tetrahydrofuran, dichloromethane) (Earnshaw et al. 1979; Gassman et al. 1993; Russell and Hegedus 1983). However, it is also possible to synthesize alkyl enol ethers **3** starting from aldehydes **1**, by acetalization with an alcohol under acid catalysis, then elimination of alcohol, under acid or basic catalysis (Rhoads et al. 1970). The elimination step is usually conducted under aggressive Brønsted acids, such as sulfuric acid or *p*-toluenesulfonic acid (Rhoads et al. 1970) or readily hydrolysable Lewis acids such as aluminum chloride (Barbot and Miginiac 1979). This step can also be accomplished under co-catalysis with aluminum chloride and a non-nucleophilic base, such as triethylamine (Barbot and Miginiac 1979). The conditions are contrary to the principles of green chemistry.

Since the infrared characterization of Eco-Mn_1 by desorption of pyridine has shown the existence of Lewis and Brønsted acidities for the catalyst, we decided to investigate the efficiency of Eco-Mn_1 to catalyze the formation of ethyl enol ether. The reaction was conducted with Eco-Mn_1 (amount corresponding to 10 mol% of Mn) in anhydrous ethanol at 80 °C, with aliphatic aldehydes as model substrates (Scheme 1 and Table 3).

Aliphatic acetals **2a** and **2b** were obtained in good yields (77–96 %) after 5 h. It is interesting to note that when the reaction was conducted on ketones, no trace of ketal was detected, the starting ketone remaining unchanged. This is in accordance with the less electrophilic character of ketones in comparison with aldehydes. The alcohol elimination of the resulting acetals led to the formation of the corresponding ethyl enol ethers **3a**, **3b** in good yields (82–89 %). The diastereomeric ratio of *E*/*Z* were similar to those previously reported (Barbot and Miginiac 1979), the more stable *Z* diastereomer being slightly preponderant.

When citronellal was used as the aldehyde substrate, enol ether **3c** was obtained directly and in good yield (96 %) after 5 h. It is interesting to note that no trace of acetal was detected. The elimination of the intermediate acetal has been facilitated by Eco-Mn_1. According to IR studies above mentioned, Eco-Mn_1 presented both Lewis and Brønsted acid characters. This induced a great affinity toward O-ethyl groups and promoted the elimination step. Eco-Mn_1 thus proved to be a valuable alternative to classical acid catalysts used for the synthesis of ethyl enol ethers, avoiding the use of strong acid catalysts or sensitive reagents. As Eco-Mn_1 was partially soluble in the reaction medium, its incorporation into a solid support could be the subject of further study, enabling its recovery by filtration and possibly its recycling, at the end of the reaction.

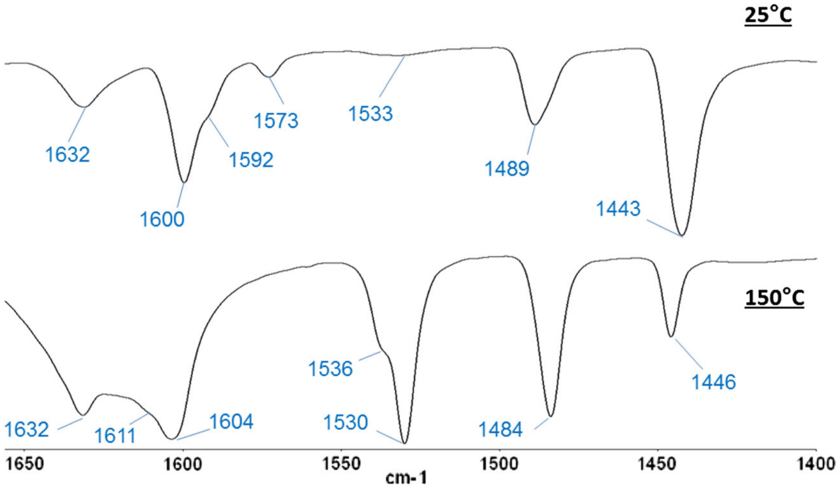
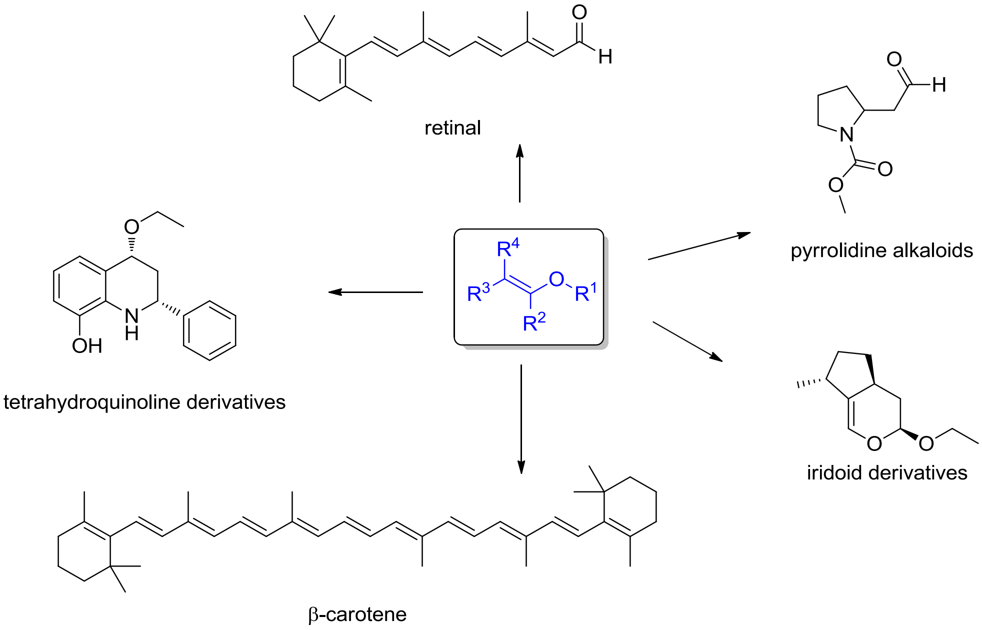


Fig. 5 IR spectra of pyridine adsorbed on Eco-Mn_1 recorded following outgassing at the indicated temperatures

Fig. 6 Examples of compounds synthesized with alkyl enol ethers



Carbonyl-ene cyclization of citronellal into isopulegol The ene-cyclization of the monoterpene (+)-citronellal into (−)-isopulegol is the main step of the best industrial process for (−)-menthol production, which is worldwide one of the most important flavor chemicals (Clark 2007; Lawrence and Hopp 2006). (−)-Isopulegol is also used in perfumery in various blossom compositions as geranium notes.

As the skeleton of the (−)-isopulegol molecule has two new stereogenic centers compared to (+)-citronellal, this intramolecular carbonyl-ene reaction can lead to four diastereomers namely (−)-isopulegol, (+)-iso-isopulegol, (+)-neo-isopulegol, and (+)-neoiso-isopulegol (Fiege 2012). Among the four pairs of optical menthol enantiomers, only (−)-menthol exhibits the characteristic peppermint odor and also exerts a cooling effect. As only (−)-isopulegol affords the correct (−)-menthol configuration during its selective hydrogenation, its synthesis from (+)-citronellal requires a high diastereoselectivity (ds).

It is known that the isomerization of (+)-citronellal occurs in the presence of various homogeneous and heterogeneous acid catalysts and the most selective catalysts toward the formation of (−)-isopulegol are Lewis acids (Imachi et al. 2007). Brønsted acidity enhances the rate of isomerization of citronellal but is less selective toward the formation of (−)-isopulegol (Da Silva et al. 2004; Kropp et al. 1995). The selectivity of this cyclization is directly related to the strength of the Lewis acid metal centers. It depends also on solvent and reaction temperature.

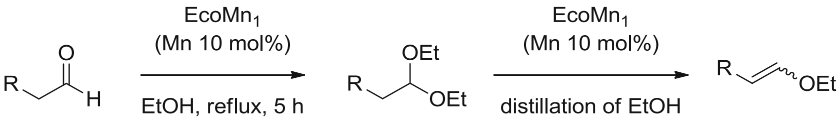
According to the hard and soft acids bases (HSAB) theory (Ho 1975), Mn^{2+} is a hard Lewis acid and can advantageously replace $AlCl_3$, $FeCl_3$, and BF_3 in a number of reactions such as the ene-reaction. However, its use is limited by a low reactivity. The polymetallic composition of Eco-Mn_1 and the presence of cations such as Fe^{3+}, and Al^{3+} could exalt the classical reactivity of Mn^{2+}. Thus, the ecocatalyst could provide an interest in the catalysis of the carbonyl-ene reaction. We decided to evaluate the efficiency of Eco-Mn_1 as catalyst for the reaction.

As described in the literature (Imachi et al. 2007), the best selectivity was obtained in dichloromethane (e.g. rather than toluene). Eco-Mn_1 catalyzed efficiently the reaction in dichloromethane, giving 95 % yield and a selectivity of 90 % toward (−)-isopulegol, with only 2 mol% of Mn, in very short reaction time (0.5 h) (Fig. 7).

The selectivity toward the isomer of interest, (−)-isopulegol, is higher with Eco-Mn_1 than those obtained with others transition metal chlorides such as: $ZnCl_2$, $FeCl_3$, $TiCl_4$, $SnCl_4$, $SbCl_3$ (Nakatani and Kawashima 1978) $InCl_3$, $NbCl_5$, $TaCl_5$ (Andrade et al. 2004), and $CuCl_2$ (Alaerts et al. 2006).

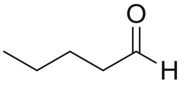
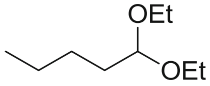
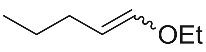
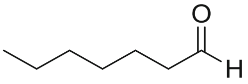
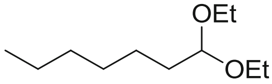
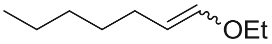
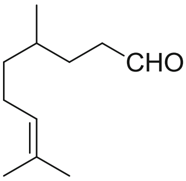
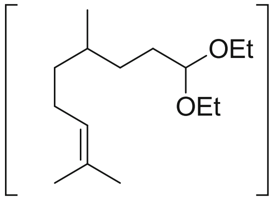
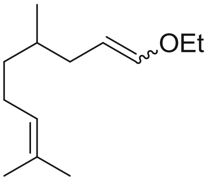
The rate of 90 % is important, because it allows avoiding the purification of the mixture for its industrial utilization. This result shows that Eco-Mn_1 is an efficient catalyst for the carbonyl-ene reaction and could replace advantageously classical Lewis acids. Moreover, as Eco-Mn_1 proved to be insoluble in the reaction medium, its recovery by simple filtration then washing was possible. After drying under

Scheme 1 General concept of acetalization/elimination of aldehydes catalyzed by Eco-Mn_1



1 **2** **3**

Table 3 Acetalization/elimination of aldehydes catalyzed by Eco-Mn_1

Entry[a]	Aldehyde	Acetal	Yield (%)[b]	Enol ether	Yield (%)[b]	*E*/*Z*[c]
1	 **1a**	 **2a**	96	 **3a**	89	47/53
2	 **1b**	 **2b**	77	 **3b**	82	26/74
3	 **1c**	 **2c**		 **3c**	96	nd[d]

[a] Reaction conditions: aldehyde (1.0 mmol), Eco-Mn_1 (82 mg, amount corresponding to 10 mol% of Mn), anhydrous ethanol (3 mL), 80 °C, 5 h

[b] Yield was determined by GC-MS with biphenyl as internal standard

[c] Proportions of diastereomers were determined by GC-MS, according to Barbot and Miginiac (Barbot and Miginiac 1979)

[d] The GC separation of diastereomers was insufficient to determine their proportions

reduced pressure, the recycled Eco-Mn_1 could be reused in the reaction without significant loss of activity.

Eco-Mn_2: a versatile biosourced oxidation reagent

As described in the previous sections, the manganese-hyperaccumulating plant *G. exul rubiginosa* is a valuable vegetal source of manganese. Eco-Mn_1 proved to be an effective Lewis acid catalyst, because its polymetallic composition increased its catalytic properties. In this section, we consider *G. exul rubiginosa* for preparing a Mn(IV)-derived biosourced oxidation reagent, named Eco-Mn_2.

Oxidation of organic compounds by Mn(IV) species, mainly under the form of manganese dioxide, has long been known in organic synthesis (Cahiez et al. 2001a; Fatiadi 1976a, b; Fatiadi 1986; Taylor et al. 2005). MnO_2 displays several advantages as a green oxidation reagent: this compound is non-toxic, widely available, and cheap. However, the oxidizing capacity of MnO_2 is modest and it is seldom used synthetically. MnO_2 needs to be prepared under active form for displaying its oxidizing activity. Moreover, even under the active form, oxidation reactions with MnO_2 require a large excess of oxidant (typically 10 equivalents). The development of simple and sustainable methods of preparation of active Mn(IV) are thus useful.

With Mn(II) species from *G. exul rubiginosa* on hand, we were able to develop a novel method of preparation of active Mn(IV) by the mean of dioxygen from air, yielding Eco-Mn_2 as an efficient and biosourced oxidation reagent. The preparation of Eco-Mn_2 was based on the oxidation by dioxygen from air at pH 8, of Mn(II) from Eco-Mn_1 into Mn_2O_3 (Mn(III)) and Mn_3O_4 (Mn(II,III)), then into Mn(IV) and Mn(II) by disproportionation, after acidification at pH 3, according to the following equations:

$$Mn_3O_4 + 2H^+ \rightarrow Mn^{2+} + Mn_2O_3 + H_2O \tag{1}$$

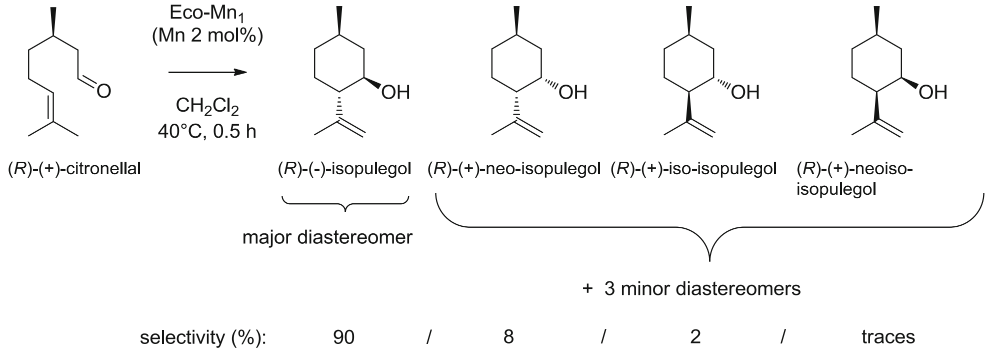
$$Mn_2O_3 + 2H^+ \rightarrow Mn^{2+} + MnO_2 + H_2O \tag{2}$$

Characterization of Eco-Mn_2

In order to use Eco-Mn_2 in organic synthesis, its elemental composition has been investigated by ICP-MS, after dissolving the solid in aqua regia (concentrated nitric acid/hydrochloric acid, 1:3) then dilution with an aqueous solution of 2.5 % nitric acid (Table 4).

The analysis shows that Mn is by far the major metallic element present in Eco-Mn_2, as its content reaches 48.22 wt%.

Fig. 7 Carbonyl-ene cyclization of (+)-citronellal into isopulegol under catalysis with Eco-Mn_1



The value can be compared to the Mn content in pure MnO_2, which is 63.19 wt%. The difference between the two values is explained by the presence of Fe in significant proportions (6.79 wt%) and by traces of other metallic elements, mainly Ca (2.85 wt%). Because of the acidification by hydrochloric acid, Cl is also present under the form of metallic chlorides, but the amount of this element could not be established by the analysis. The percent of recovery of each element from Eco-Mn_1 has been calculated by using the data in Table 1, with the masses of the starting Eco-Mn_1 (50 mg) and of the resulting Eco-Mn_2 (5.5 mg). These values show that Mn, Fe, and Ni were recovered efficiently (78.93–96.25 % recovery), whereas high proportions of Mg, Ca, and Al were lost during the preparation of Eco-Mn_2, probably during the washing with water (1.48–35.75 % recovery). The resulting Eco-Mn_2 is thus highly enriched in Mn (under the form of MnO_2 and Mn(II) chlorides) and Fe (under the form of Fe(III) chlorides). It should be noted that the Mn/Fe ratio in Eco-Mn_2 is almost the same as for Eco-Mn_1 (Mn/Fe, 7.47 in Eco-Mn_1; 7.10 in Eco-Mn_2).

The preparation of Eco-Mn_2 by disproportionation of Mn_2O_3 (Mn(III)) and Mn_3O_4 (Mn(II,III)) produced Mn(IV) and Mn(II) species (see Eqs. 1 and 2). Attempts to determine the Mn(II)/Mn(IV) ratio by X-ray photoelectron spectroscopy (XPS) were unsuccessful, because of the complexity of the observed signals. We thus made an estimation of the Mn(II)/Mn(IV) ratio based on the two extreme cases: if Mn_3O_4 (Mn(II,III)) is the major oxide formed by oxidation with air, the Mn(II)/Mn(IV) ratio (after disproportionation) is equal to 2; if Mn_2O_3 (Mn(III)) is the major oxide formed by oxidation, then the Mn(II)/Mn(IV) ratio (after disproportionation) is equal to 1. The actual Mn(II)/Mn(IV) ratio is therefore comprised between these two extreme values. Supplementary spectroscopic study of Eco-Mn_2, which proved to be a quite complex material, is under progress in our laboratory.

Considering this composition, Eco-Mn_2 should prove interesting properties in oxidation reactions involving Mn(IV) as the oxidizing species, with assistance of Mn(II) and Fe(III) chlorides as Lewis acids and as potential sources of Brønsted acidity (by hydrolysis in presence of hydrated salts, as observed with Eco-Mn_1). Because of a specific IR absorption of Eco-Mn_2 without pyridine, between 1500 and 1630 cm^{-1}, the characterization of Eco-Mn_2 by pyridine adsorption could not provide information. Only a slight band at 1445 cm^{-1} was observed as a proof of the Lewis acidity of Eco-Mn_2. A slight Brønsted acidity was indicated by a positive test of Eco-Mn_2 on wet pH indicator paper. pH measurement of a suspension of Eco-Mn_2 (10 mg in 20 mL of water) indicated a value of 6.5. In addition, the acidity of Eco-Mn_2 was clearly indicated by the results obtained in organic reactions detailed below.

Unlike Eco-Mn_1, Eco-Mn_2 could not be characterized by XRD analysis, because of the amorphous structure of the solid obtained. This is in accordance with previously described observations about the form of MnO_2 prepared by precipitation procedures, as most of the methods led to amorphous solids which could not be characterized by XRD (Fatiadi 1986).

Examples of Eco-Mn_2-promoted oxidations

Oxidation of allylic and benzylic alcohols into aldehydes To start our investigations on the oxidation of organic substrates with Eco-Mn_2, we selected the oxidation of benzyl alcohol **4a** into benzaldehyde **5a** as a model reaction (Scheme 2).

Oxidation of benzyl alcohol to benzaldehyde is an important chemical reaction, as benzaldehyde is one of the most industrially useful compounds. Commercially, the oxidation of benzyl alcohol in liquid phase is a common route for the manufacture of benzaldehyde. Numerous oxidizing agents are available to effect this key reaction, as it is an important transformation in synthetic organic chemistry. Although several stoichiometric reagents based on activated dimethyl sulfoxide (Swern oxidation) (Lee 1991), hypervalent iodine compounds (Dess-Martin periodinane) (Dess and Martin 1983), and reactive oxo-metal compounds (Ley and Madin 1991) (MnO_2 and pyridinium chlorochromate) have been developed, the search for new catalytic procedures for selective oxidations of benzylic or allylic alcohols remains an area of intensive interest. Indeed, in spite of their efficiency, the drawback of such oxidants in the perspective of their use in multistage organic synthesis is their lack of selectivity. For instance, over-oxidation of aldehydes into carboxylic acids

Table 4 Elemental composition of Eco-Mn_2 and recovery of the elements from Eco-Mn_1

Ecocatalyst	Mg wt% (±sd)	Ca wt% (±sd)	Al wt% (±sd)	Mn wt% (±sd)	Fe wt% (±sd)	Ni wt% (±sd)
Eco-Mn_2 from *Grevillea exul rubiginosa*	0.71 (±0.0019)	2.85 (±0.0015)	0.78 (±0.0028)	48.22 (±0.0012)	6.79 (±0.0024)	0.35 (±0.0027)
Percent of recovery of the element from Eco-Mn_1 (in %)	1.48	3.00	35.75	78.93	82.99	96.25

and degradation of unsaturated substrates are often unavoidable side reactions. Furthermore, high temperatures and presence of strong acids or bases required by some oxidation procedures often leads to detrimental side reactions.

As described in Table 5, entry 1, the plant-derived Eco-Mn_2 allowed the quantitative formation of benzaldehyde with less than 4 molar equivalents of Mn. The amounts of Mn species were small compared to the classical conditions (typically, 10 equivalents (Cahiez et al. 2001a)). This example illustrates the advantage of using manganese-hyperaccumulating species to replace the commercial oxidizing reagent MnO_2.

Different explanations could explain the result. First, the high oxidizing activity of Eco-Mn_2 may result to the controlled disproportionation of Mn_2O_3 and Mn_3O_4 into active MnO_2, realized during the preparation of Eco-Mn_2. Secondly, the original and polymetallic composition of the medium (particularly Fe(III) species) may exalt the oxidizing power of Mn(IV) while controlling the reaction to the expected aldehyde stage. In order to learn more about these results, it was of interest to study the reactivity of the mixture of commercial MnO_2 and $FeCl_3$. In the previous conditions, only 20 % of benzaldehyde was obtained (Table 5, entry 3). This result clearly indicated that the combination of Mn(IV) and Fe(III) cannot explain the observed yield. It may be concluded to a synergetic effect between the present species. At the end of the reaction, a black solid of similar aspect than the starting Eco-Mn_2 was recovered by filtration. After washing and drying, a reaction was attempted with this recycled Eco-Mn_2. Almost no oxidation of the starting alcohol was observed, which is in accordance with the reduction of Mn(IV) during the first run, probably into Mn(II). This could constitute a complementary way to prepare a new catalyst, highly enriched in Mn(II), by reduction of Eco-Mn_2 whose content in Ca, Mg, and Al is much lower than in Eco-Mn_1. Other reducing reagents, compliant with green chemistry principles, such as $FeCl_2$ could also be envisioned for the reduction of Mn(IV) of Eco-Mn_2 into Mn(II).

The absence of benzoic acid among the reaction products constituted a proof to assess the mildness of this oxidation procedure. This advantage was illustrated with the oxidation of 4-hydroxy-3-methoxybenzyl alcohol (vanillic alcohol). The reaction was also very effective with Eco-Mn_2 (Table 5, entry 4). It led to vanillin in a remarkably simple and efficient green process. This result is of great industrial importance, as vanillin is the most consumed flavor in the world. This synthesis is completely bio-based: the precursor alcohol is a natural and abundant substance in a number of plant species such as *Picea sitchensis* (Pinaceae) (Buckingham 1994); the oxidant is completely natural, as prepared from plant extract. Such synthesized vanillin can be described as natural vanillin flavor (Stanzione et al. 2012).

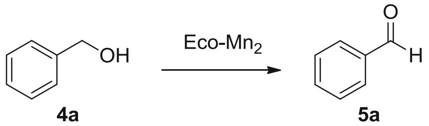
This oxidation reaction is easily transposable to the controlled oxidation of allylic alcohols under similar conditions. This possibility is illustrated with the example of geraniol which leads to geranial (*trans*-citral) (Table 5, entry 5) which faces high demand for its lemon scent in the food industry or as an important intermediate for the production of perfumes, fragrances, and pharmaceuticals (Hoelderich and Kollmer 2000) (Scheme 3).

Encouraged by these results, the oxidation of the polyol **6** was carried out with the aim to study the regioselectivity of the reaction. In view of its multifunctionality, the derivative **6** was an interesting model substrate. The presence of polyol, the cyclic furan, and the carboxylic ester moiety were an opportunity to know the behavior of Eco-Mn_2 (Scheme 4).

The reaction was followed by ^1H NMR. Surprisingly, we observed the presence of a characteristic singlet at 9.7 ppm by ^1H NMR. After work-up, the conjugated aldehyde **7** was identified.

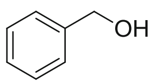
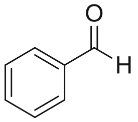
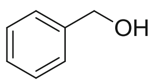
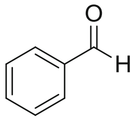
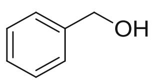
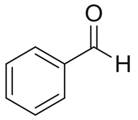
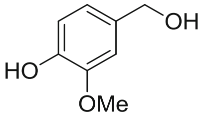
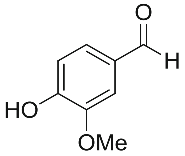
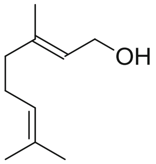
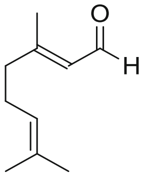
The quantitative formation of **7** was attained with 6 equivalents of Mn from Eco-Mn_2, and 5 h of agitation at room temperature in acetonitrile. We could conclude that Eco-Mn_2 promoted the oxidative cleavage of the polyol **6** in the benzylic position. The reaction showed no competing side reactions, which confirmed the excellent regioselectivity of the cleavage. We found that the control of the oxidation conditions was optimal, since the aldehyde **7** was not oxidized further.

The yield of the reaction is markedly higher with Eco-Mn_2 in comparison with Ce(IV) reagents, which needed a large excess of oxidant (11 equivalents, 48 % yield) (Moreno-Vargas et al. 2001).



Scheme 2 Controlled oxidation of benzylic alcohol with Eco-Mn_2 into benzaldehyde

Table 5 Oxidation of alcohols by Eco-Mn_2

Entry	Alcohol	Oxidizing reagent[a]	Product	Yield (%)[b]
1	 **4a**	Eco-Mn_2	 **5a**	100
2	 **4a**	MnO_2	 **5a**	traces
3	 **4a**	$MnO_2 + FeCl_3$[c]	 **5a**	20
4	 **4b**	Eco-Mn_2	 **5b**	100
5	 **4c**	Eco-Mn_2	 **5c**	100[d]

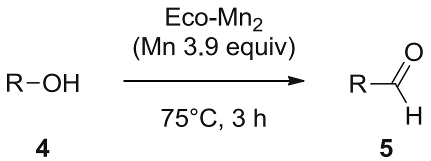
[a] Reaction conditions: alcohol (10 mmol), Mn from Eco-Mn_2 or from commercial MnO_2 (38.9 mmol), EtOAc (20 mL), 75 °C, 3 h

[b] Yield determined by GC-MS with biphenyl as internal standard

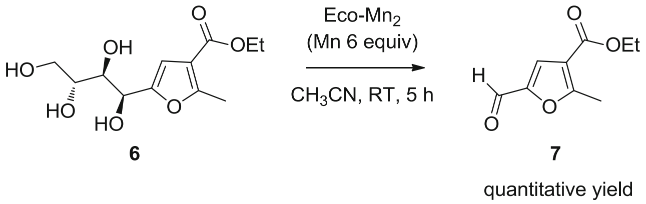
[c] An amount of 5.30 mmol of $FeCl_3$ was used, in order to reproduce the ratio Mn/Fe of Eco-Mn_2

[d] Greater than 95 % *trans*-citral is obtained

The oxidative cleavage of vicinal polyols is a reaction of great synthetic importance, mainly applied to the fission of 1,2 diols (glycols) (Perlin 2006). The nature of the conventional reagents illustrated the importance of the result obtained with Eco-Mn_2. Periodic acid and its salts and lead tetraacetate are the most commonly used reagents for the oxidative cleavage of glycols, but several others have been described and reviewed. The following are examples of reagents used for the transformation: $NaBiO_3$, Ce(IV) reagents, sodium and calcium hypochlorite, Cr(VI), Co(II), or V(IV) reagents, and *N*-iodosuccinimide (Shing 1991). Although these reagents are effective in the reaction, most of them are highly toxic or unstable and generate problematic wastes, excluding their use in a sustainable perspective. More recently, methodologies implying the use of O_2 as oxidizing reagent have been developed, under catalysis with ruthenium (Takezawa et al. 1999), palladium (Wang and Jiang 2010), or cobalt species (Iwahama et al. 2000). Although these methods represent valuable green improvements in oxidative cleavage of glycols, the catalysts involved are based on rare and expensive metals, limiting their use. Among the reagents described for the reaction, one could



Scheme 3 General concept of the oxidation of alcohols by Eco-Mn_2



Scheme 4 Oxidation of polyhydroxyalkyl furan 6 by Eco-Mn_2

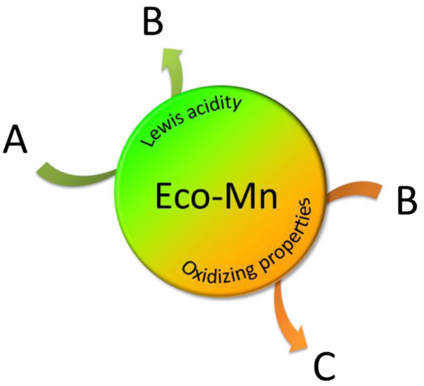


Fig. 8 General concept of sequential tandem oxidations catalyzed by Eco-Mn

also notice a brief mention of MnO_2, apparently untapped later in spite of its high efficiency (Ohloff and Giersch 1973).

As even with activated commercial MnO_2 a large excess of reagent is needed (typically more than 30 equivalents (Ohloff and Giersch 1973)), we made the hypothesis that the superior activity of Eco-Mn_2 is due to the presence of Lewis acids (Mn(II) and Fe(III) chlorides), promoting the formation then the opening of the cyclic intermediate probably involved in the mechanism, as previously reported for sodium periodate or lead tetraacetate (Perlin 2006). The involvement of such cyclic intermediate is supported by the previous experimental conclusions made by Ohloff and Giersch, when they described that only 1,2-*cis*-diols or flexible 1,2-*trans*-diols can be cleaved by MnO_2 (Ohloff and Giersch 1973). Only one study has mentioned the use of MnO_2 in the reaction since the work of Ohloff and Giersch, but without mechanistic considerations on the oxidative cleavage (Outram et al. 2002). Because of this almost-absence in the literature of experimental data on the mechanism of the MnO_2-oxidative cleavage of glycol, this could be the object of a further study.

The oxidative cleavage of polyhydroxyalkyl furan **6** into furanic aldehyde **7** could be an interesting way to produce functionalized furfural-derived compounds, with new functionalities compared to the widely studied furfural (Serrano-Ruiz et al. 2011) and 5-hydroxymethylfurfural (Rosatella et al. 2011).

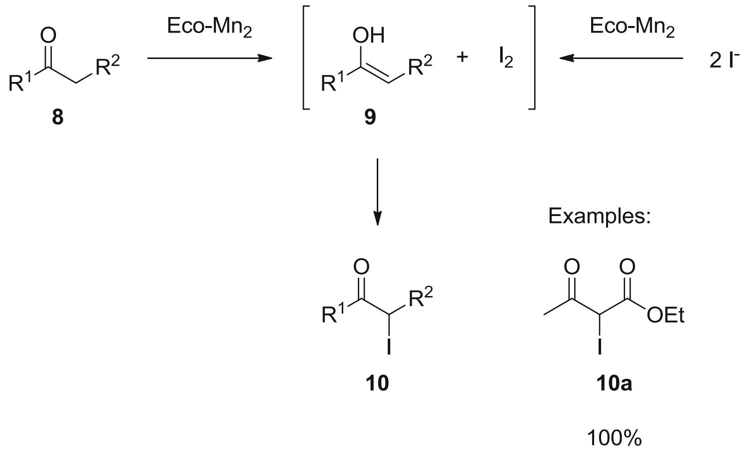
Eco-Mn: Janus catalysts for sequential tandem oxidations

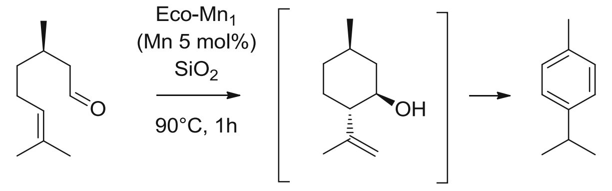
Sequential tandem oxidations can be described as multistep processes, in which transformation of the substrate occurs via two (or more) mechanistically distinct processes, one of them being an oxidation, thanks to the action of species already present at the beginning of the reaction (Fogg and Dos Santos 2004). Because tandem processes reduce the number of operations and allow reactive intermediates to be prepared and reacted in situ, avoiding their isolation and often preventing safety problems, such processes are consistent with the green chemistry principles (Anastas and Warner 1998).

Transition elements are frequently involved in tandem oxidation processes, as they often combine different chemical properties acting in the different steps of the sequential reaction (Davi and Lebel 2009; Guo et al. 2009; Wang et al. 2010; Yip et al. 2006). Among these elements, manganese is the object of a number of publications devoted to tandem oxidations, mainly with Mn(III) (Li et al. 2011; Snider 1996; Snider and O'Hare 2001; Tanyeli et al. 2002; Tanyeli and Sezen 2000) and Mn(IV) (McAllister et al. 2006; Quesada et al. 2006; Quesada and Taylor 2005; Taylor et al. 2005).

In the previous sections, we have shown that Eco-Mn_2 demonstrates both oxidizing properties and Lewis/Brønsted acidity. We decided thus to investigate the potential of Eco-Mn_2 in sequential tandem oxidations, as a "Janus catalyst" (a previously described type of material with two different catalytic properties, from the two-faced Roman god Janus (Cobo et al. 2012; Lv et al. 2012)). The reactions we considered involve two different steps, one being conducted under Lewis or Brønsted acid catalysis and the other one consisting in an oxidation. Such reactions are usually performed with two different species: a catalyst and an oxidizing reagent. Being able to combine these two activities in one unique material offers great advantages in a sustainable perspective, with

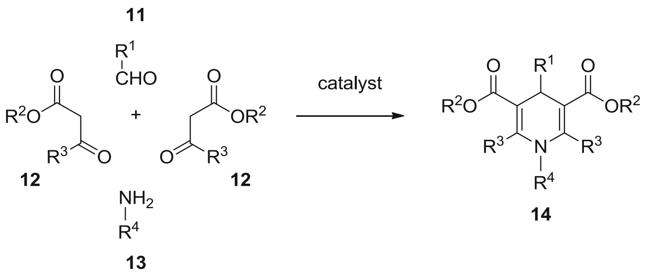
Scheme 5 Direct oxidative iodination of ketones with NaI/Eco-Mn_2





(R)-(+)-citronellal (R)-(-)-isopulegol p-cymene

Scheme 6 Tandem ene reaction/dehydration/oxidation of (+)-citronellal into *p*-cymene



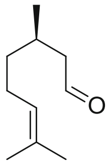
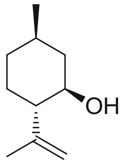
Scheme 7 The multicomponent Hantzsch reaction

reduction of wastes and simplification of processes. During the course of these studies, we also discovered that Eco-Mn$_1$, previously described only as a Lewis and Brønsted acid catalyst, could catalyze oxidation reactions, with dioxygen from air. The following examples illustrate thus the potential of the two Eco-Mn$_1$ and Eco-Mn$_2$ as Janus catalysts for sequential tandem oxidations (Fig. 8).

Oxidative iodination of ketones with Eco-Mn$_2$ Halogenated compounds are widely used as chemical precursors in a number of reactions (Meijere and Diederich 2004). In particular, α-iodinated ketones exhibit great reactivity and give access to a large set of compounds, including heterocycles with pharmacological activity (Erian et al. 2003).

Among the classical methods of synthesis of α-iodoketones (De Kimpe and Verhé 2010), some of the most frequently used imply the formation of electrophilic derivatives of iodine, by using I$_2$ in combination with various oxidizing reagents, such as SeO$_2$ (Bekaert et al. 2000), Ce(IV) ammonium nitrate (Horiuchi and Kiji 1988), or *m*-iodosylbenzoic acid (Yusubov et al. 2010). In spite of their efficiency, these methods make use of toxic or unstable oxidizing reagents, often inconsistent with the requirements of the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) regulation (European Commission 2006). Moreover, as I$_2$ is a quite aggressive compound, its manipulation is problematic, especially on large scale. For example, the utilization of I$_2$ is strongly discouraged in industrial processes of iodination (Adams et al. 2013). For these reasons, various groups have proposed new methodologies implying the in situ formation of electrophilic species of iodine by oxidation of iodides, which are safe compounds (e.g., NaI, KI or NH$_4$I). Examples include the use of NaI/H$_2$O$_2$/H$_2$SO$_4$ (Barluenga et al. 2004), KI/air/H$_2$SO$_4$/NaNO$_2$ (Stavber et al. 2008), or NH$_4$I/Oxone® (Reddy et al. 2011). Even if these methods represent significant improvements, they still make use of corrosive acids (H$_2$SO$_4$) or very toxic compounds (NaNO$_2$). We thus decided to examine the potential of Eco-Mn$_2$ in this reaction, as an alternative and safe oxidizing reagent, with NaI as iodine source.

Table 6 Formation of *p*-cymene with Eco-Mn$_1$

Entry	Terpene	Catalyst[a]	Yield (%)[b]
1		Eco-Mn$_1$ 0.05 equiv. of Mn	80
2		Eco-Mn$_1$ 0.15 equiv. of Mn	91

[a] Reaction conditions: terpene (1.0 mmol), silica gel (100 mg), Eco-Mn1, 90 °C, 1 h

[b] Yield was determined by GC-MS with biphenyl as internal standard

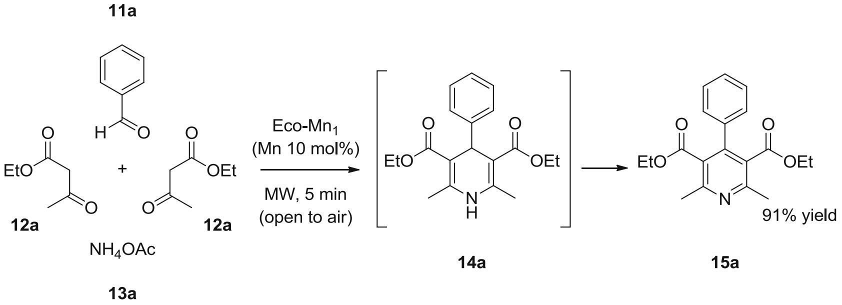
Thanks to its Lewis and Brønsted acidity, Eco-Mn$_2$ promoted the enolization of the ketone **8**. At the same time, the oxidizing properties of Eco-Mn$_2$ allowed the in situ formation of I$_2$, present in the reaction medium only as a temporary intermediate which was immediately consumed by reaction with the enolized ketone **9**, forming the α-iodoketone **10** (Scheme 5).

By using two equivalents of Mn from Eco-Mn$_2$ under agitation at room temperature for 12 h, the reaction was quantitative on β-dicarbonyl compounds. Under the same conditions, cyclohexanone was directly iodinated to give 2-iodocyclohexanone **10b** in 64 % yield, confirming the activity of the system on less easily enolizable ketones. Eco-Mn$_2$ is thus a valuable green alternative to more noxious or unstable oxidizing reagents, avoiding the use of strong acids and toxic species.

*Tandem carbonyl-ene cyclization and aromatization of citronellal to **p**-cymene*

The transformation of natural biomass materials (e.g., terpenes) into value-added chemical and fine chemical products, as recently described by Corma et al. (2007), is highly important, and such conversion via green catalytic processes remains a considerable challenge. Here, we describe the unexpected conversion of (+)-citronellal (biosourced starting material, cf. "Lewis/Brønsted acid catalysis with Eco-Mn1") into *p*-cymene under catalysis with silica-supported Eco-Mn$_1$, in a solvent-free methodology.

Scheme 8 Tandem DHP synthesis-oxidation into pyridine, catalyzed by Eco-Mn$_1$

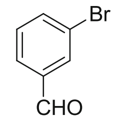
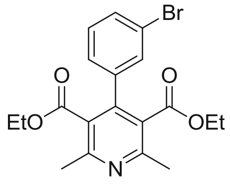
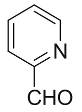
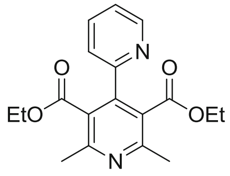
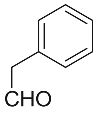
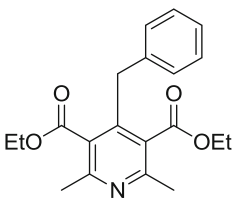


p-Cymene is used in a lot of industrial applications, as intermediate for the production of pesticides, fungicides, flavors, and pharmaceuticals (Fiege 2012; Roberge et al. 2001) or as a ligand in hydrogenation catalysts, such as [(η_6-cymene)RuCl$_2$]$_2$ (Tada et al. 2010). Currently, *p*-cymene is mainly produced by the Friedel–Crafts alkylation of toluene with 2-propanol and acid catalysts such as AlCl$_3$ and HCl (Eggersdorfer 2012). This reaction is performed at high temperatures (≥200 °C), produces unwanted isomers and multialkylation products, so that the yield of *p*-cymene usually does not exceed 50 % (Barman et al. 2005). Moreover, the use of large amounts of hazardous acid catalysts and solvents gives rise to many problems, such as handling, safety, waste disposal, and corrosion, and are becoming more restricted by environmental legislation in industrialized countries. Thus, new pathways that avoid the continued use of these toxic reagents should be found.

Here, we propose an elegant one-pot and solvent-free process, starting from (+)-citronellal and leading to *p*-cymene. With a catalytic loading of only 5 mol% of Mn from Eco-Mn$_1$, dispersed on silica as solid medium, *p*-cymene was formed in 80 % yield from (+)-citronellal, after heating to 90 °C for 1 h (Scheme 6 and Table 6, entry 1).

Eco-Mn$_1$ catalyst was used with the degree of oxidation of Mn present in the plant, i.e., Mn(II), but Mn(II) species are devoid of oxidizing properties and therefore cannot explain the observed aromatization. This result may be due to the presence of traces of oxidizing species such as Mn(III) or Mn(IV) in the *G. exul rubiginosa*-derived catalyst. Eco-Mn$_1$ acted thus as a Janus catalyst, enabling to perform the

Table 7 The scope of the tandem DHP synthesis-oxidation into pyridine with Eco-Mn$_1$

Entry	Aldehyde	Product[a]	Yield (%)[b]
1	 **11b**	 **15b**	69
2	 **11c**	 **15c**	89
3	 **11d**	 **15d**	96

[a] Reaction conditions: Eco-Mn$_1$ (amount corresponding to 0.05 mmol of 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

[b] Isolated yield

carbonyl-ene reaction of (+)-citronellal into isopulegol (thanks to its Lewis acidity, as demonstrated by our previous infrared study), followed by dehydration of isopulegol into a cyclic alkene (catalyzed by the Brønsted acidity of Eco-Mn_1, equally shown by the infrared study), then by aromatization into *p*-cymene, probably through a Mn(III) or Mn(IV)-catalyzed oxidation (O_2 from air being the terminal electron acceptor). As Eco-Mn_1 was initially conceived to contain Mn only under the form of Mn(II) species, we suppose that the traces of Mn(III) or Mn(IV) were formed by oxidation with O_2 from air. Previous studies have indeed shown that whereas the oxidation of Mn(II) into Mn(III) or Mn(IV) by O_2 from air is a very slow process, this transformation is highly accelerated in presence of traces of Fe(III) (Diem and Stumm 1984; Luther 2005). As Eco-Mn_1 contains 0.90 wt% of Fe(III), the formation of such traces of Mn(III) or Mn(IV) in Eco-Mn_1 by oxidation of Mn(II) with O_2 from air is thus possible. Fe(III) being a oxidizing agent too, it is equally possible that this species participates with Mn(III) or Mn(IV) in the catalyzed oxidation.

Very few articles in the literature tell about the transformation of isopulegol into *p*-cymene, and these rare methods are not adapted to preparative synthesis (Bestmann et al. 1986). In order to validate the formation of *p*-cymene from isopulegol, we tested the action of Eco-Mn_1/SiO_2 catalysis on (−)-isopulegol. *p*-Cymene was thus obtained with an excellent yield of 91 % (Table 6, entry 2).

This sequential tandem reaction is specific of Eco-Mn_1 catalysis, where the evolution of isopulegol during its formation is unusual. None of the multitude of articles related to *p*-cymene synthesis refers to start from citronellal or isopulegol. This ecocatalyzed methodology is therefore the first to give access to *p*-cymene thanks to a sequential tandem oxidation combining three steps (carbonyl-ene reaction/dehydration/aromatization) in one procedure. For these reasons, the method is in agreement with sustainable chemistry, especially with respect to the green chemistry principles that refer to the elimination of hazardous solvents and reagents, to energy efficiency and to the utilization of renewable raw materials (Anastas and Warner 1998). Work is under progress to further enlarge the scope and the mechanistic description of this methodology.

Pyridine synthesis by Hantzsch reaction-aromatization with Eco-Mn_1

Another example of sequential tandem oxidation is the direct synthesis of pyridines, obtained by oxidation of 1,4-dihydropyridines resulting of the Hantzsch reaction.

1,4-Dihydropyridines (DHPs) have attracted the interest of the scientific community, because of their potential in various research fields. DHPs are indeed widely used as biomimetic reducing agents of a large set of chemical functions, thanks to their similarity with physiological hydrogen-transferring co-enzymes (Liu et al. 2009; Nakamura et al. 1984; Rueping et al. 2005). Moreover, DHPs exhibit a number of pharmacological activities (Edraki et al. 2009). The rapid progress in synthesis and applications of DHP is regularly reported in review papers (Eisner and Kuthan 1972; Lavilla 2002; Saini et al. 2008; Stout and Meyers 1982; Wan and Liu 2012).

The multicomponent Hantzsch reaction (Scheme 7), described in 1882 (Hantzsch 1882), is one of the methods described for synthesizing DHP **14**, under Brønsted or Lewis acid catalysis. Previously described catalysts include $Bi(NO_3)_3{\cdot}5H_2O$ (Bandyopadhyay et al. 2012), I_2 (Ko et al. 2005), *p*-toluenesulfonic acid (Cherkupally and Mekala 2008), montmorillonite K10 (Zonouz and Hosseini 2008), $RuCl_3$ (Suresh and Sandhu 2009), or $Yb(OTf)_3$ (Wang et al. 2005).

As Eco-Mn_1 was successfully used in acid-catalyzed reactions (see "Lewis/Brønsted acid catalysis with Eco-Mn1"), we decided to examine its efficiency in the Hantzsch synthesis of DHP. We chose to test Eco-Mn_1 as catalyst of the reaction under microwave irradiation, after dispersion of the catalyst and reagents on silica gel. Surprisingly, we obtained only trace amounts of DHP **14a**, but the corresponding pyridine **15a** was formed in 91 % yield (Scheme 8). As the reaction was performed in the presence of air, we assumed that the DHP **14a** was synthesized thanks to the acid catalysis of Eco-Mn_1 and then oxidized into pyridine **15a** by O_2 from air.

However, when using the same conditions, but starting from the corresponding DHP **14a**, without addition of Eco-Mn_1, the DHP proved to be quite stable during heating, with formation of only 22 % of the pyridine **15a**. This result proves that the oxidation of DHP into pyridine results from the catalytic oxidizing activity of Eco-Mn_1, which may be due to the presence of traces of the oxidizing species Fe(III) and/or of Mn(III) or Mn(IV) in Eco-Mn_1, as described in the previous section (tandem carbonyl-ene cyclization and aromatization of citronellal). This is consistent with a previous report of oxidation of DHP into pyridines by Mn(IV), but in stoichiometric conditions (Vanden Eynde et al. 1995).

This reaction has been extended to some other structures, illustrating the scope of the methodology (Table 7).

Eco-Mn_1 thus proved to be a very efficient catalyst for the tandem DHP synthesis-oxidation by O_2 from air. This system could advantageously replace the classical oxidizing reagents used for the synthesis of pyridines from DHP, such as SeO_2 (Cai et al. 2005), Ce(IV) ammonium nitrate (Pfister 1990), HIO_3 or I_2O_5 (Chai et al. 2006), HNO_3-bentonite (Garcia et al. 1993), or $KMnO_4$ (Vanden Eynde et al. 1994), some of which may be inconsistent with the new environmental legislations because of their toxicity. Moreover, whereas these oxidizing reagents are used in stoichiometric proportions, Eco-Mn_1 allows their substitution by a greener catalytic methodology involving O_2 from air as green oxidizing reagent.

Conclusion

G. exul rubiginosa grown on degraded mining sites proved to be a valuable source of Mn for chemical synthesis applications. By deliberately simple procedures, two plant-based extracts highly enriched in Mn were produced and characterized. ICP-MS and XRD analyses revealed that the Eco-Mn extracts contained original polymetallic complexes, which may account for the particular reactivity of these plant-based extracts in green synthesis. Eco-Mn_1 displayed marked Lewis and Brønsted acidities which make it a very efficient catalyst in the preparation of ethyl enol ethers (82–96 % yield) and in the carbonyl-ene cyclization of (+)-citronellal into isopulegol (95 % yield), with a higher selectivity toward (−)-isopulegol (90 %) than a number of commercial Lewis acid catalysts. Eco-Mn_2 was produced by a simple procedure of oxidation of Mn(II) from Eco-Mn_1 into Mn(IV), by using air as a green oxidizing reagent. The resulting Eco-Mn_2 demonstrated the efficiency of an activated form of MnO_2, strengthened by the presence of Lewis acids (Mn(II) and Fe(III) chlorides) formed during its preparation. As a result, Eco-Mn_2 was used as a green and efficient oxidizing reagent for the controlled oxidation of allylic and benzylic alcohols into aldehydes and for the oxidative cleavage of a polyol in quantitative yield. Finally, the two Eco-Mn_x acted as Janus catalysts by promoting sequential tandem oxidation reactions, thanks to their content in Lewis acids and oxidizing species. The new reactivity of Eco-Mn developed here was especially motivating since conventional and classic oxidative agents are strongly discouraged by REACH regulation. The resulting methodology combined these two activities in one unique material, offering great advantages in a sustainable perspective, with reduction of wastes and simplification of processes. Further experimentation would be required in order to fully determine the potential and the mechanistic action of the new plant-based catalysts, but there is no doubt that they will display very interesting properties for cutting-edge green chemistry, while contributing to the development of phytoremediation programs.

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