Ecocatalysis for 2H-chromenes synthesis: an integrated approach for phytomanagement of polluted ecosystems

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Abstract A direct, general and efficient method to synthesize 2*H*-chromenes (2*H*-benzo[*b*]pyrans), identified as environmentally friendly pesticides, has been developed. This approach lays on the new concept of ecocatalysis, which involves the use of biomass from phytoextraction processes, as a valuable source of metallic elements for chemical synthesis. This methodology is similar or superior to known methods, affording 2*H*-chromenes with good to excellent yields (60–98 %), including the preparation of precocene I, a natural insect growth regulator, with 91 % yield. The approach is ideal for poor reactive substrates such as phenol or naphthol, classically transformed into 2*H*-chromenes by methodologies associated with environmental issues. These results illustrate the interest of combining phytoextraction and green synthesis of natural insecticides.

Keywords Metal hyperaccumulating plants · Phytoextraction · Biopesticides · Chromenes · Ecocatalysis · Green chemistry

Introduction

According to Freedonia Group (2010), global demand for pesticides will rise 2.9 % annually to 2014. Gains will reflect a reversal of declines in 2009, caused in part by a price drop for the leading herbicide, glyphosate. Herbicides and insecticides will remain the largest types. Asia and South America will offer the best growth opportunities. Demand for formulated pesticides in the agricultural market in China is forecast to rise 5.3 % per annum to 2.3 million metric tons in 2015. In value terms, formulated pesticide demand is expected to rise 7.1 % per year to 60 billion Yuan. Market gains will be driven primarily by increases in agricultural production as measured by the total area of sown land and ongoing expansions in the production of fruits and vegetables, which are by far the most intensive users of pesticides relative to most other crops.

This study analyzes the $45 billion pesticide industry at the global scale. It presents historical demand data for the years 1999, 2004, and 2009 and forecasts it for 2014 and 2019 by-product (herbicides, insecticides, and fungicides), market (wheat, corn, rice, soybeans, consumer, and commercial), and world region and for 39 major countries.

According to these data, globalization promotes the development of invasive species. For instance, devastation caused by the Asian Formosan subterranean termite (*Coptotermes formosansus*, Rhinotermitidae) in North America has been estimated to cost $US 1 billion a year. Over the past two decades, organochlorines and organophosphates, the two prominent classes of termite control agents, have been banned, owing to environmental and human health concerns (Meepagala et al. 2010). In each case, there is an increased need to discover effective, environmentally friendly, and safe insect control agents with minimal human and environmental toxicity.

In addition, the pesticide pollution is sometimes exacerbated by metallic pollution of soils. Indeed, mining activities and agriculture practices lead to the contamination of soils and surface waters by metallic trace elements and pesticides. It is admitted that significant levels of pollution have been reached, inducing food contamination and human health risks.

On the other hand, Zn phytoextraction provides coherent and workable responses to the problems of large-scale revegetation and phytoremediation and may, ultimately, contribute

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to the ecological restoration of contaminated mine sites (Wu et al. 2012). The development of these advanced techniques will help accomplish the remediation of marginalized lands polluted by heavy metals. For example, in France and southern China, our group and collaborators are performing phytoextraction of Zn-polluted soils (Saunier et al. 2013; Wu et al. 2013). A similar methodology is developed for Mn phytoextraction in New Caledonia on degraded mining sites, thanks to accumulation abilities of local plants (Brooks et al. 1981; Jaffre 1977, 1979). However, phytoextraction generates a new waste, namely the contaminated biomass. The treatment of contaminated leaves appears thus as an environmental problem again.

This paper has the ambition to propose an innovative technology to tackle these two types of pollution. The concept is based on the pioneering idea that metallic wastes recycled from hyperaccumulating plants can be used for the production of green, bioinspired pesticides. Our group already established a new concept that the biomass from phytoextraction can receive a new value, thanks to its transformation into ecocatalysts for the synthesis of organic molecules (Escande et al. 2014a, b, c; Grison et al. 2013; Losfeld et al. 2012a, b, c; Thillier et al. 2013). In this paper, we planned to study the use of these ecocatalysts for the synthesis of green pesticides, reinforcing the ecological interest of the technology. Our aim is to demonstrate that ecocatalysis represents an extraordinary environmental opportunity for the plant-based synthesis of bioinspired and green pesticides. By combining phytoextraction and ecocatalysis, we describe a novel access to emerging biopesticides, eco-friendly substitutes to toxic pesticides.

Model candidate molecules have been chosen in order to limit their human and environmental toxicity. We focused on juvenile hormone inhibitors in insects such as cockroach (*Periplaneta americana* Blattidae) (Pratt and Bowers 1977) and milkweed bug (*Oncopeltus fasciatus* Lygaeidae) (Brooks et al. 1979). Such juvenile hormonal inhibitors of natural origins include plant-based 2*H*-chromenes with insecticidal activities (Proksch et al. 1983; Proksch and Rodriguez 1983).

Several articles and patents have been published, concerning the biological activity, mechanism of action, and metabolism of natural 2*H*-chromenes, specifically precocenes (Adler and Baldwin 2009; Brooks et al. 1979; Lv et al. 2012; Timar et al. 1983). Exposure of young larval stages of test insects to precocenes leads to precocious metamorphosis into unviable adults. Precocenes constitute a new type of insect growth regulator and have been referred to as *fourth-generation insecticides*. They are considered as environmentally friendly and have been postulated as biocontrol agents (Bowers et al. 1976; Lévai et al. 1990; Triseleva 2003). Our objective will be to develop a green process based on the use of ecocatalysts, which are efficient and low cost and can be used on an industrial scale.

The retrosynthetic strategy revealed that these molecules can be accessed by a cascade reaction, which involves the electrophilic addition of a phenol aromatic ring to an enal, followed by the dehydration of adduct and then by an intramolecular 6π-electrocyclization (Adler and Baldwin 2009; Dintzner et al. 2006) (Scheme 1).

Materials and methods

Ecocatalyst preparation

The selection of hyperaccumulating plants was undertaken in the context of our ongoing phytoremediation programs. Zn-hyperaccumulating plant leaves were derived from *Noccaea caerulescens* (Brassicaceae). They were collected from plants growing on the Les Avinières mine site, at Saint-Laurent-le-Minier (Gard) in the Mediterranean climate region of southern France. Mn-hyperaccumulating plant leaves derived from *Grevillea exul rubiginosa* were collected from plants growing in the southern province of New Caledonia (Thio).

Leaves were harvested before flowering, air-dried, and grounded. The obtained solid (30 g) was calcinated at 400 °C for 5 h, and the resulting powder (5 g) was added to 50 mL of a solution of hydrochloric acid (~1 M). The solution was heated at 60 °C and stirred for 2 h. The reaction mixture was then filtered on celite. The resulting solutions were then concentrated under vacuum. The resulting ecocatalysts were stored under nitrogen atmosphere. Purification steps are not mandatory in our process.

Inductively coupled plasma mass spectrometry (ICP-MS) analyses were performed using the metal analysis of total dissolved solutes in water, in order to determine the composition of the ecocatalyst obtained. 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 analyzes were performed for each sample in order to determine the standard deviation of the measurement. Results are summarized in Table 1.

Scheme 1 Retrosynthetic analysis for access to 2*H*-chromenes
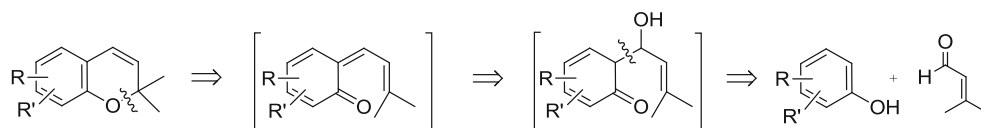
Table 1 Metallophyte species and derived ecocatalyst

Ecocatalyst	Mg wt% (±sd)	Ca wt% (±sd)	Al wt% (±sd)	Mn wt% (±sd)	Fe wt% (±sd)	Zn wt% (±sd)	Pb wt% (±sd)	Cd wt% (±sd)
Eco-Zn from *Noccaea caerulescens*	3.76 (±0.10)	35.81 (±0.50)	1.74 (±0.049)	0.071 (±0.0027)	1.80 (±0.028)	6.57 (±0.059)	0.73 (±0.0048)	0.35 (±0.0040)
Eco-Mn from *Grevillea exul rubiginosa*	5.26 (±0.086)	10.44 (±0.17)	0.24 (±0.015)	6.72 (±0.037)	0.90 (±0.0075)	0.06 (±0.0025)	nd	nd

nd not determined (<10 ppm)

Synthesis

Chemicals

Reagents and solvents were purchased from Sigma-Aldrich and were used without further purification. All reactions were performed under nitrogen atmosphere and magnetic stirring unless otherwise noted. When needed, glassware was dried overnight in an oven (T>100 °C).

Purification and analysis of reaction products

Gas chromatography and mass spectrometry (GC-MS) analyses were performed using electronic impact ionization mode on a Varian Saturn 2000 ion trap instrument, interfaced with a Varian CP-3800 apparatus. The Varian CP-3800 was equipped with a 1079 split-splitless injector (206 °C) and a 30 m× 0.25 mm×0.25 μm film thickness ID WCOT CPSil-8CB-fused silica capillary column (Chrompack®, Bergen op Zoom, The Netherlands), with helium as carrier gas (1 mL/min), and was programmed for 2 min isothermal at 50 °C, then increasing from 50 to 220 °C at 4 °C/min. Mass spectra were recorded in electronic impact (EI) at 70 V and were identified by comparison with data of the NIST 98 software library (Varian, Palo Alto, CA, USA) and by comparison of the retention time of the standard compounds.

Flash column chromatography was performed using Chromagel Carlo Erba Reactifs SDS silica 60A CC 35–70 μm. Reactions were monitored using Merck Kieselgel 60 F254 aluminum. TLCs were visualized by UV fluorescence (254 nm) and then by immersion into KMnO₄ or vanillin ethanolic solutions.

NMR spectra were recorded on a Brüker Avance 300 spectrometer at room temperature, ¹H frequency is at 300 MHz, and ¹³C frequency is at 75 MHz. IR spectra were recorded on a PerkinElmer Spectrum 100 FT-IR spectrometer, in ATR mode. Mass spectra were determined with a LC-MS Waters 3695 Separation module, Micromass ZQ 2000 by electrospray ionization (ESI positive or negative mode).

Experimental conditions of synthesis under ecocatalysis

The following syntheses involving the ecocatalysts were conducted in various reaction conditions, such as conventional heating or microwave (MW) activation. The experimental conditions are not necessarily dependent upon the use of a microwave oven. They can be performed in more conventional conditions. Specific examples are described below; the conditions are adapted to the involved reaction mechanisms and the difference in reactivity of the nucleophilic substrate.
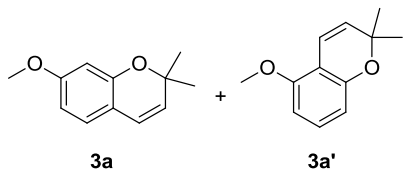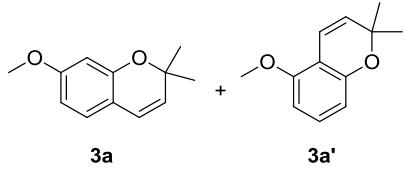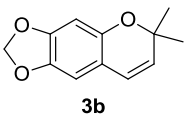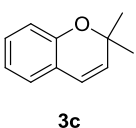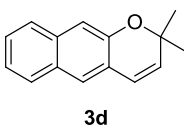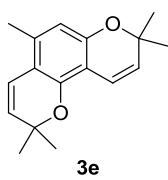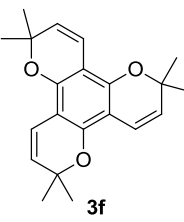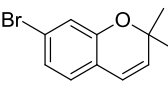
Chromenes synthesis – Procedure with electron-rich substituted phenol derivatives

In a sealed tube, 0.1 mmol of electron-rich phenolic derivatives, 0.8 mmol of 3-methyl-2-butenal, 150 mg of 4 Å activated molecular sieves, 10.1 mg of Eco-Zn (0.01 mmol in Zn), and 2 mL of anhydrous toluene were introduced. The mixture was stirred for 2–4 h at 110 °C (reaction progress followed by GC-MS analysis). 2*H*-chromenes were isolated after washing with dichloromethane, and filtration, concentration under reduced

Scheme 2 Synthesis of 2*H*-chromenes with Eco-Zn catalyst
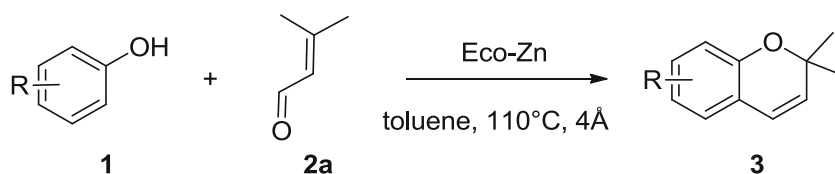
Table 2 Scope of the Eco-Zn-catalyzed synthesis of 2*H*-chromenes

Entry	Product[a]	Eco-Zn (equiv of Zn)	Time (h)	Yield %[b] (regioisomers ratio)
1	**3a** + **3a'**	0.1	2	91 (82)[c] (**3a/3a'** = 95/5)
2	**3a** + **3a'**	0.1	2	62[d] (**3a/3a'** = 95/5)
3	**3b**	0.1	4	98 (76)[c]
4	**3c**	1.0	20	60
5	**3d**	1.0	20	73
6	**3e**	0.1	4	95
7	**3f**	0.1	4	92
8	**3g**	1.0	20	1

[a] Reaction conditions: phenol derivative (0.1 mmol), 3-methyl-2-butenal (0.8 mmol), 4 Å activated molecular sieves (150 mg), Eco-Zn (amount corresponding to indicated values), anhydrous toluene (2 mL), 110 °C

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

[c] Isolated yield

[d] Eco-Zn was supported on montmorillonite K10

Table 3 Test of various Lewis acid catalysts in precocene I synthesis

Entry	Lewis acid catalyst[a]	Catalyst equivalents	Yield %[b]	3a/3a′ regioisomers ratio[b]
1	Eco-Zn	0.1 (Zn)	91	95/5
2	ZnCl$_2$	0.1	23	97/3
3	CaCl$_2$	0.1	1	nd[c]
4	FeCl$_3$·6H$_2$O	0.1	11	89/11
5	MnCl$_2$·4H$_2$O	0.1	1	nd[c]
6	Zn(CF$_3$SO$_3$)$_2$	0.1	49	94/6
7	Ca(CF$_3$SO$_3$)$_2$	0.1	0	nd[c]
8	Fe(CF$_3$SO$_3$)$_3$	0.1	1	nd[c]
9	Mn(CF$_3$SO$_3$)$_2$	0.1	12	98/2

[a] Reaction conditions: 3-methoxyphenol (0.1 mmol), 3-methyl-2-butenal (0.8 mmol), 4 Å activated molecular sieves (150 mg), Lewis acid catalyst (0.01 mmol), anhydrous toluene (2 mL), 110 °C, 2 h

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

[c] Not determined

pressure, and then chromatographic purification on silica gel were performed with a hexane/ethyl acetate mixture (9:1) as an eluent. They were identified by comparison with previously reported spectral data (Iyer and Trivedi 1990; Lee et al. 2005; Lykakis et al. 2011).

– Procedure for low reactivity derivatives: phenol, naphthol, and 3-bromophenol

In a sealed tube, 0.1 mmol of phenol, 0.8 mmol of 3-methyl-2-butenal, 150 mg of 4 Å activated molecular sieves, 101 mg of Eco-Zn (0.1 mmol in Zn), and 2 mL of anhydrous toluene were introduced. The mixture was stirred for 20 h at 110 °C and was then submitted to the previously described treatment. The structure of compounds was determined by full spectroscopic characterization and was identified by comparison to previously published spectral data (Kureshy et al. 2009; Zeng et al. 2011).

Cannabinoid synthesis Representative procedure with sesamol

In a scintillation tube, 0.5 mmol of sesamol, 0.55 mmol of citral, 50 mg of Eco-Zn (0.05 mmol of Zn), and

montmorillonite K10 (500 mg) were introduced. The mixture was placed in a microwave oven for 8 min (mechanic stirring after 1 min) at 500 W. After washing with dichloromethane, filtration, concentration under reduced pressure, and then chromatographic purification on silica gel were performed with a hexane/ethyl acetate mixture (9:1) as an eluent, and 6*H*-benzo[*b,d*]pyran,6*a*,7,10,10*a*-tetrahydro-6,6,9-trimethyl-1,3-benzodioxole (**6a**) was isolated as red oil with 90 % yield [IR cm^{-1} 1,478, 1,629, 2,907; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 1.14 (s, 3H), 1.38 (s, 3H), 1.64–1.70 (m, 1H), 1.75 (s, 3H), 1.88–2.01 (m, 2H), 2.13 (m, 1H), 2.52 (brdd, J=16.6 Hz, 5.3 Hz, 1H), 2.63 (dt, J=11.2 Hz, 5.3 Hz, 1H), 5.48 (m, 1H), 5.86 (m, 2H), 6.36 (s, 1H), 6.69 (s, 1H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 18.3, 22.9, 27.0, 27.1, 32.2, 36.5, 42.6, 76.5, 98.5, 100.2, 105.1, 116.8, 119.6, 132.8, 140.8, 145.9, 147.3].

Results and discussion

The methodology was based on catalysis with Eco-Zn, with or without supporting on montmorillonite K10 (according to previously described procedures) (Laszlo and Mathy 1987; Nasreen 2001). The mixture of aldehyde and phenol derivatives was added to the catalytic system, and then, the reaction was carried out at 110 °C in anhydrous toluene. Experiments aimed at examining the possibility of catalyzing 2*H*-chromenes synthesis (Scheme 2) with this ecocatalyst gave interesting results. Table 2 presents the data obtained.

The results clearly show the interest of ecocatalysis. The performances of our ecocatalysts are at least similar (entry 3) and even higher (entries 1, 5, 6, and 7) than previous methodologies, allowing the synthesis of 2*H*-chromenes (Adler and Baldwin 2009; Dintzner et al. 2006; Lee et al. 2005; Pettigrew et al. 2005; Tiabi and Zamarlik 1991; Zeng et al. 2011). Moreover, the catalysis by Eco-Zn avoids the use of harsh conditions and sensitive reagents previously reported (Sartori et al. 1979). We tried to perform the reaction under heterogeneous catalysis, by supporting Eco-Zn on montmorillonite K10, but this was associated with a slight loss of yield (entry 2).

It is interesting to note that entries 1–3 led to precocene derivatives. Precocene I (**3a**) is a natural insecticide with anti-juvenile hormone activity in insects (Brooks et al. 1979). Eco-Zn catalysis allows its synthesis with high yield (91 %) and selectivity (95 %). The efficiency of the Eco-Zn catalyst in

Scheme 3 Lewis acid-catalyzed synthesis of precocene I (**3a**)
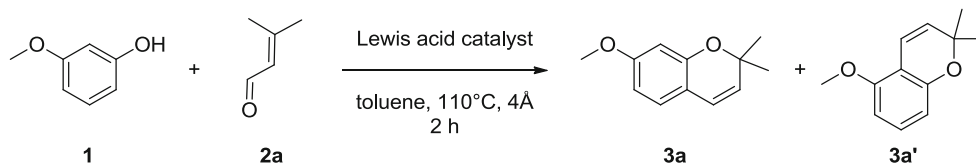
precocene I (**3a**) synthesis was highlighted by a comparison with various commercial Lewis acids derived from Zn, Fe, Mn, and Ca, under the form of chlorides and trifluoromethanesulfonates (triflates), often used as powerful Lewis acid catalysts (Table 3).

Among the tested Lewis acid catalysts, Eco-Zn clearly showed the highest activity (91 % yield, entry 1), followed by Zn triflate (49 % yield, entry 6) and then by Zn chloride (23 % yield, entry 2). Notable degradation was observed with Ca and Fe triflates, resulting in almost no formation of the expected products (entries 7 and 8). Most of the catalysts displayed a high selectivity toward **3a** regioisomer, but only Eco-Zn was able to combine simultaneously high yield and selectivity (Scheme 3).

Under ecocatalysis, synthesis of 2*H*-chromenes was possible with various nucleophilic substrates. We show here that it is possible to extend this type of reaction to less electron-rich substrates in this type of transformation and, finally, to prepare new structures deemed inaccessible by these synthetic routes. It is important to note that nucleophiles conventionally considered to be insufficiently reactive in this type of reaction can be used here, thanks to ecocatalysis. This is, for example, the case for phenol (Table 2, entry 4) and naphthol (Table 2, entry 5), whose corresponding 2*H*-chromenes have been accessed in previous reports with toxic or non-eco-friendly catalysts such as rhenium pentacarbonyl chloride (Zeng et al. 2011), TiCl$_4$ (Sartori et al. 1979), or BF$_3$·Et$_2$O (Madabhushi et al. 2012). However, the Eco-Zn-catalyzed reaction with a substrate bearing an electron-withdrawing substituent, poorer in electrons than phenol, such as 3-bromophenol (Table 2, entry 8) gave only traces of the corresponding chromene. A similar tendance was observed by authors using a phenylboronic-acetic acid-catalyzed methodology on 4-bromophenol, isolated with 35 % yield, one of the lower reported yields in spite of prolonged heating and high loading of catalyst (Chauder et al. 1998).

The methodology can be extended to bi- or triphenolic structures (Table 2, entries 6 and 7). With 3-methyl-2-butenal, the expected 2*H*-chromenes were formed and the sequential reactions were almost quantitative.

Dienals, such as citral, were also effective in this reaction. Optimization of reaction conditions revealed that microwave irradiation proved to be much more efficient than thermal heating. Indeed, when carried under MW irradiation, the reaction was completed in 8 min, whereas more than 20 h was necessary under conventional heating, even with electron-rich substrates. By contrast with the previous 2*H*-
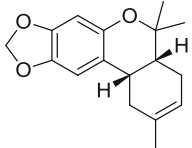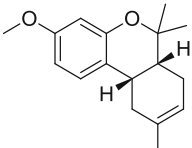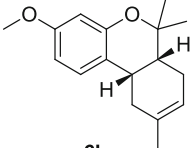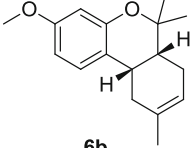
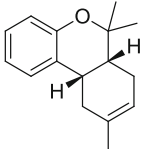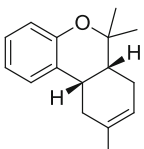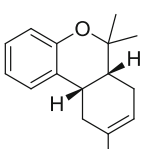chromene synthesis, the final reaction after dehydration of adduct was not an intramolecular 6π-electrocyclization, but a hetero Diels-Alder reaction, involving the terminal double bond (Scheme 4). The product obtained was not a 2*H*-chromene, but a cannabinoid-related structure (Table 4). Interestingly, structure **6** was formed in situ after migration of the C=C double bond of the initially expected structure **5** which is not isolated. Structure **6** is suggested by the ^{1}H NMR signal of the olefinic proton, at 5.48 ppm, which would have been deshielded to values superior to 6 ppm in structure **5**, because of an induced diamagnetic field arising from the aromatic ring, as already described on similar compounds (Choi et al. 2004; Taylor et al. 1966). The coupling constant of protons at cycle junction (*J*=5.3 Hz) indicated a *cis* configuration. No *trans* form was detected during analysis of the reaction products. This result shows the interest of the methodology, giving access with high selectivity to structures similar to natural products such as Δ^8-tetrahydrocannabinoids derivatives (Goujon et al. 2002).

Results in entries 1 and 2 show that irradiating the mixture for 8 min allows to obtain high yields of products. The yield can be increased to 98 % when the time reaction was nearly doubled (15 min instead of 8 min), according to entries 2 and 3. As montmorillonite K10 was used as a solid medium for the reaction, we investigated the catalytic activity of the sole clay. It appeared that only 20 % of the product was formed in these conditions, demonstrating that the efficiency of the methodology is due to the Eco-Zn catalyst. However, for less electron-rich substrates like phenol, the previous conditions did not lead to the same efficiency (10 % yield, entry 5). We then investigated for a better ecocatalyst by using Eco-Mn. The yield was then slightly increased when using Eco-Mn in the same conditions (20 % yield, entry 6). After optimization of the reaction conditions, we were able to obtain the cannabinoid **6c** in 72 % yield, by using an excess of citral and one equivalent on Mn from Eco-Mn. It is important to note that the synthesis of cannabinoid **6c** was not previously described under Lewis acid catalysis in the literature, probably because of the low activation of the starting aromatic ring. Moreover, the ecocatalyst efficiency can be pointed out by comparison with previous catalytic systems such as dichlorophenylboranes which led to lower yield (30 %) of the product similar to **6b** (Kun Lau et al. 1993). Ecocatalysis allowed equally the access to new structures, such as the cannabinoid **6a** whose synthesis was not previously described.

Scheme 4 Extension of the reaction sequence to dienal
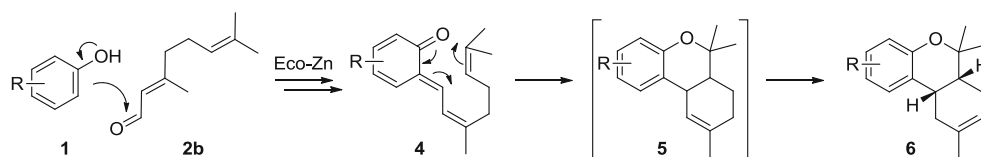
Table 4 Scope of the methodology with dienal (citral)

Entry	Product[a]	Ecocatalyst	Time (min)	Yield %[b]
1	**6a**	Eco-Zn (0.1 equiv Zn)	8	97 (90)[c]
2	**6b**	Eco-Zn (0.1 equiv Zn)	8	92 (68)[c]
3	**6b**	Eco-Zn (0.1 equiv Zn)	15	98
4	**6b**	–	8	20[d]
5	**6c**	Eco-Zn (0.1 equiv Zn)	8	10
6	**6c**	Eco-Mn (0.1 equiv Mn)	8	20
7	**6c**	Eco-Mn (1 equiv Mn)	8	72[e]

[a] Reaction conditions: phenol derivative (0.5 mmol), citral (0.55 mmol), Eco-Zn (amount corresponding to indicated values) and montmorillonite K10 as solid medium (500 mg), MW irradiation at 500 W

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

[c] Isolated yield

[d] Montmorillonite K10 only, without ecocatalyst

[e] Eight equivalents of citral were used

Conclusion

The aim of this work was to describe an efficient green access to the emerging biopesticides, which are eco-friendly substitutes to conventional toxic pesticides. It was possible to access complex benzopyrans, some of which are natural products belonging to the chromene group, in good to excellent yields. These molecules were prepared by ecocatalysis, an innovative methodology involving the use of biomass from phytoextraction processes as a valuable source of metallic elements for catalysis. Eco-Zn and Eco-Mn catalysts were able to promote addition reactions on enals and dienals of various reactivities with phenol nucleophiles. Moreover, this methodology provides an efficient access to cannabinoid-related structures, including the new product **6a** which could find an interest in further studies.

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