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Solvent-free transesterification of methyl levulinate and esterification of levulinic acid catalyzed by a homogeneous iron(III) dimer complex

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ABSTRACT

Levulinic acid esters $MeC(O)CH_2CH_2CO_2R$ (**LAE**) are emerging bio-based chemicals used as solvents, additives and plasticizers. In this work a variety of levulinates (R = *n*-butyl, *n*-hexyl, *n*-octyl, 2-ethylhexyl, geranyl, 2-ethoxyethyl, benzyl, 2-octyl, cyclohexyl, menthyl) is obtained from the solvent-free transesterification of methyl levulinate (**ML**) and esterification of levulinic acid (**LA**), catalyzed by a dimeric complex of iron(III). The results are competitive with the few related reports of literature mainly based on heterogeneous catalysis. This first systematic study based on a homogeneous catalytic system therefore represents a significant extension within the field of biomass valorization.

1. Introduction

The synthesis of chemicals must be re-formulated to fully embrace the circular economy, and especially those of great industrial interest should be derived from renewable resources or, better, from waste. In this contest, biomass is a powerful resource [1]. One of its most abundant fraction is the lignocellulosic portion (LCB) that is becoming a main source of raw material, due to its abundance, availability and variety of chemical compounds derivable from. Among these, levulinic acid (**LA**) and its derivatives are raising scientific and industrial interest as renewable chemical platforms [2]. In particular, levulinate esters (**LAE** in Scheme 1) already cover many roles in industry [3], as solvents, additives, plasticizers and other. The presence of the additional carbonyl group allows further transformation and derivatizations for the synthesis of different libraries of compounds [4].

Both **LA** and its methyl ester **ML**, that can be directly derived from biomass [5], are convenient starting materials for the synthesis of **LAE**, according to reactions a) and b) of Scheme 1.

The reactions are equilibria, and the relative constants often favor the reactants [6]. Therefore, their driving force consists in the progressive removal of water or methanol. Moreover, the presence of a catalyst is necessary to have acceptable reaction rates. Transesterification a) is a powerful method, often advantageous compared to the direct esterification of acids b), because methyl esters are more manageable, in terms of stability and solubility [7]. Sometimes the use of acids as a starting compounds may be preferable, because they are immediately available and less volatile, so they raise fewer safety issues.

Literature offers rare hints of transesterification of methyl levulinate (in Table 1) and, besides numerous examples of direct esterification of levulinic acid with ethanol or butanol [8], also esterification with heavier alcohols is poorly represented (Table 2 lists the examples relevant to this study). These few reports generally refer to heterogeneous acid catalysis [9], frequently limited by incomplete conversions, high alcohol : LA ratios, significant catalyst loadings, use of solvents or auxiliaries.

Recently, our research group became active in the conversion of biomass into solvents and chemicals promoted by homogeneous transition metal complexes [19]. In the course of these studies, we came across an iron(III) dinuclear complex (**c1** in Fig. 1) that effectively promote benchmark transesterification reactions. [20]

On these bases, we have extended our interests to the solvent-free synthesis of levulinate esters of industrial utility using the dinuclear complex **c1** as homogeneous catalyst. Transesterification of **ML** (reaction a of Scheme 1) proceeds with high conversions even with secondary alcohols, and the comparison with the corresponding

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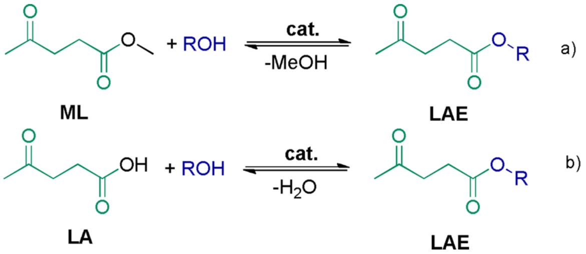


Scheme 1. Transesterification of methyl levulinate (a) and esterification of levulinic acid (b).

mononuclear catalyst **c2** confirms the importance of its binuclearity to enhance performance. The same catalyst **c1** promotes the direct esterification of **LA** with primary heavy alcohols according to reaction b of Scheme 1. As far as we know, this is the first systematic study based on a homogeneous [21] catalytic system for these transformations, and therefore it represents a significant extension of this emerging sector of biomass transformation.

2. Results and discussion

2.1. Transesterification of methyl levulinate (ML)

A screening of reaction conditions was carried out in the transesterification of **ML** with *n*-butanol (**1a**) promoted by **c1** and **c2** (Table 3), by varying the ratio **1a** : **ML** and the catalyst loading. The reactions were performed without solvents or auxiliary substances at 100 °C in an open system connected to a cold trap.

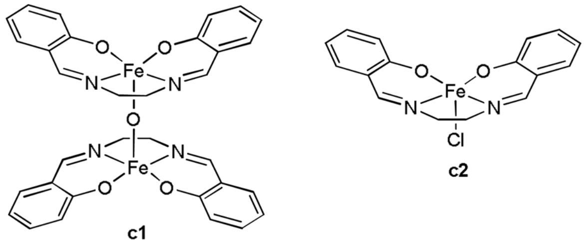


Fig. 1. Structure of complexes **c1** and **c2** used as catalysts.

Yields were evaluated by integrating appropriate regions in the NMR spectra of the reaction mixtures (e.g. Fig. 2 for entry 3). The integral of the ester protons -C(O)OCH$_x$- ($\boldsymbol{I_E}$) in the product was compared with that of one of the two methylenes of the levulinic structure ($\boldsymbol{I_L}$), which are practically coincident in the substrate and in the product: $yield = \frac{I_E/_x}{I_L/_2} \times 100$.

The data show that **c1** is very active even at low loadings (0.05 % mol/mol), while the corresponding mononuclear **c2** promotes very low yield (entry 4 vs entry 7). These results confirm that the dimeric nature of the iron(III) complexes is a decisive issue, as already disclosed by Ohshima [20].

For both catalyst loadings, increasing the molar ratio **1a**: **ML** from 1.1 : 1–1.5 : 1 improves the yields (entry 1 vs. entry 3, entry 2 vs. entry 4 of Table 3), whereas a higher value (2 : 1) has no significant beneficial

Table 1
Literature reports on transesterification of methyl levulinate (**ML**) with heavy alcohols according to Scheme 1a.

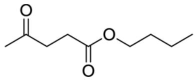
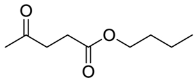
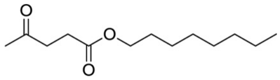
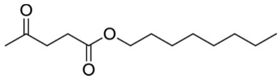
Entry (ref)	Product	Catalyst	Conditions	Yield, %
1 [10]		Sulphated SnO_2 (10% w/w)	Toluene, 110 °C, 10 h MLA : ROH 1 : 1	45
2 [11]		Amberlist 15 (10 % w/w)	Toluene, 110 °C, 10 h MLA : ROH 1 : 1	54
3 [12]		Pentafluoro-phenylammonium triflate (1 % mol/mol)	Toluene 80 °C, 24 h MLA : ROH 1 : 1.5	98
4 [13]		*p*-toluenesulfonate resin (10% w/w)	110 °C, 8h MLA : ROH 1 : 1.5	87

Table 2
Literature reports on esterification of levulinic acid (**LA**) with heavy alcohols according to Scheme 1b.

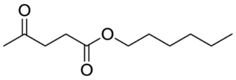
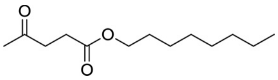
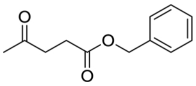
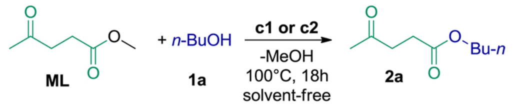
Entry (ref)	Product	Catalyst	Conditions	Yield, %
1 [8e]		Stannosilicate (10 % w/w)	120 °C, 4 h LA : ROH 1 : 3	93
2 [8d]		MIM-HSO_4 (25% mol)	90 °C, 90 min LA : ROH 1 : 2	88
3 [14]		$H_3PW_{12}O_{40}$ (10% w/w)	120 °C, 6 h LA : ROH 1 : 1.5	92
4 [15]		HPW/Al-MCM-41 (25 % w/w)	100 °C, 10 h LA : ROH 1 : 1.5	99
5 [16]		SO_3H@CGO (3% w/w)	Toluene, 110 °C, 90 min LA : ROH 1 : 1.5	95
6 [17]		GO	120 °C, 6 h LA : ROH 1 : 27	88
7 [12]		Pentafluoro-phenylammonium triflate (1 % mol/mol)	Toluene 80 °C, 2h LA : ROH 1 : 1	96
8 [13]		*p*-toluenesulfonate resin (10% w/w)	110 °C, 4 h LA : ROH 1 : 1	93
9 [18]		$HClO_4/SiO_2$ (10% w/w)	100 °C, 10 h LA : ROH 1 : 5	45
10 [16]		SO_3H@CGO (3% w/w)	Toluene, 110 °C, 90 min LA : ROH 1 : 1.5	97

Table 3
Screening of catalysts **c1** and **c2** in transesterification of **ML** with *n*-butanol (**1a**).



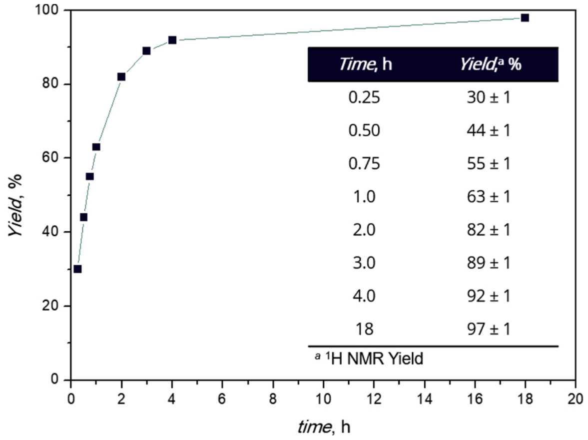
Entry	Catalyst	Cat. loading, % mol/mol	**1a** : **ML**	Yield[a] (at 18 h) [a], %
1	**c1**	0.05	1.1 : 1	71 ± 2
2	**c1**	0.5	1.1 : 1	83 ± 2
3	**c1**	0.05	1.5 : 1	80 ± 1 (95 ± 1)
4	**c1**	0.5	1.5 : 1	92 ± 1 (97 ± 1)
5	**c1**	0.05	2 : 1	80 ± 1
6	**c1**	0.5	2 : 1	93 ± 2
7	**c2**	0.5	1.5 : 1	5 ± 1

[a] Through ^{1}H NMR spectroscopy, reaction time = 4 h; T = 100 °C.

effect (entry 3 vs. entry 5; entry 4 vs. entry 6). At the optimized ratio 1.5 : 1, the catalyst loading of 0.5 % mol/mol gives better yield than 0.05 % mol/mol within 4 h (entry 3 vs entry 4), while high and comparable yields were obtained prolonging the reaction time to 18 h (entries 3 and 4 in brackets). These results improve by far those reported in literature for the same substrate (entries 1 and 2 of Table 1).

The trend of yield vs. time in the conditions of entry 4 is reported in Fig. 3, where the activity of the catalyst can be appreciated even at high reaction time. Progress of the reaction was esteemed from the evolution of the ^{1}H NMR spectra of the reaction mixture, where the progressive disappearing of the reagent signals was accompanied by growth of those pertaining to the product (Fig. 4).

Transesterification of **ML** was extended to other selected alcohols aiming to produce esters that have already demonstrated industrial applicability (Table 4). Except for the synthesis of **2c**, these reactions are described for the first time in this paper, and both catalyst loadings of 0.05 % and 0.5 % mol/mol were therefore screened in order to find customized conditions. Good to excellent yields for most of the primary alcohols were achieved within 18 h even with the lowest loading, while at 0.5 % these substrates were converted nearly quantitatively (entries 1–7). The data demonstrate the robustness of the system also in comparison with the other few examples of iron(III) homogeneous catalyzed transesterification of benchmark substrates [20,22]. The higher catalyst loading (0.5 %) was adopted with the more challenging secondary alcohols: 2-octanol, cyclohexanol and menthol were esterified with good to excellent yields (entries 8–10).



Time, h	*Yield*,[a] %
0.25	30 ± 1
0.50	44 ± 1
0.75	55 ± 1
1.0	63 ± 1
2.0	82 ± 1
3.0	89 ± 1
4.0	92 ± 1
18	97 ± 1

[a] ^{1}H NMR Yield

Fig. 3. Transesterification of **ML** with **1a** in the conditions of entry 4. Yield vs. time plot.

The efficiency of the method was also verified through the simple isolation of *n*-butyl levulinate on a larger scale. After the reaction, the mixture was filtered on a thin layer of Florisil, which was extracted with a small aliquot of ethyl acetate. The catalyst was sequestered from the column, while the eluted product was isolated after removal of the solvent under vacuum with a yield of 85 %.

2.2. Proposed catalytic cycle for transesterification

The proposed mechanism for the transesterification is sketched in Scheme 2 and is a revisiting of the mechanism described by Ohshima [20]. In excess of alcohol, the dinuclear catalyst **c1** undergoes a ligand substitution with elimination of water and formation of the bis-μ-alkoxide species **I**. One of the two bridges is then cleaved by **ML** which coordinates the iron center as in **II**. This activates the carbonyl group against the nucleophilic attack of the alkoxide ion in the proximity with the obtainment of a tetrahedral intermediate (**III**), while the position left free by the alkoxide ion is occupied by another molecule of alcohol. At this point, a sequence of electronic shifts returns the ester product and methanol, reestablishing the dinuclear species **I**.

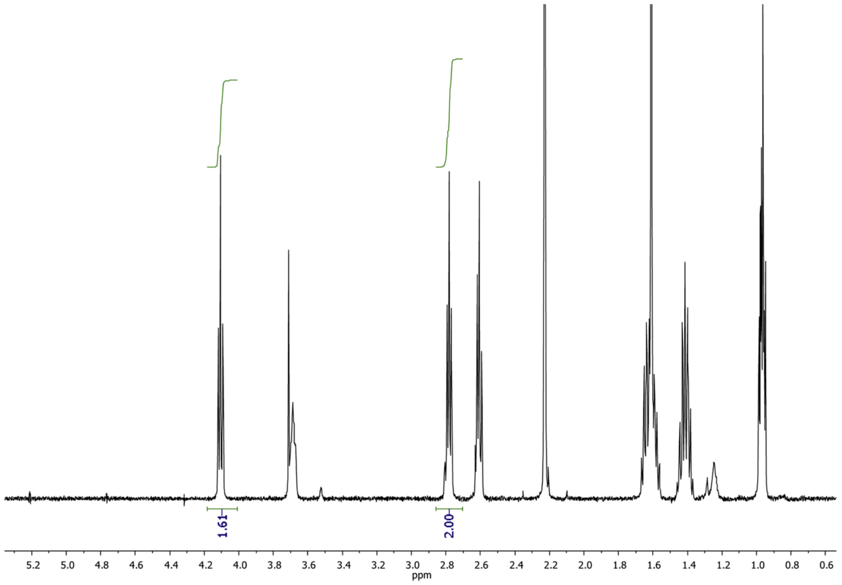


Fig. 2. Example of ^{1}H NMR spectrum for a reaction mixture (entry 3 of Table 3).

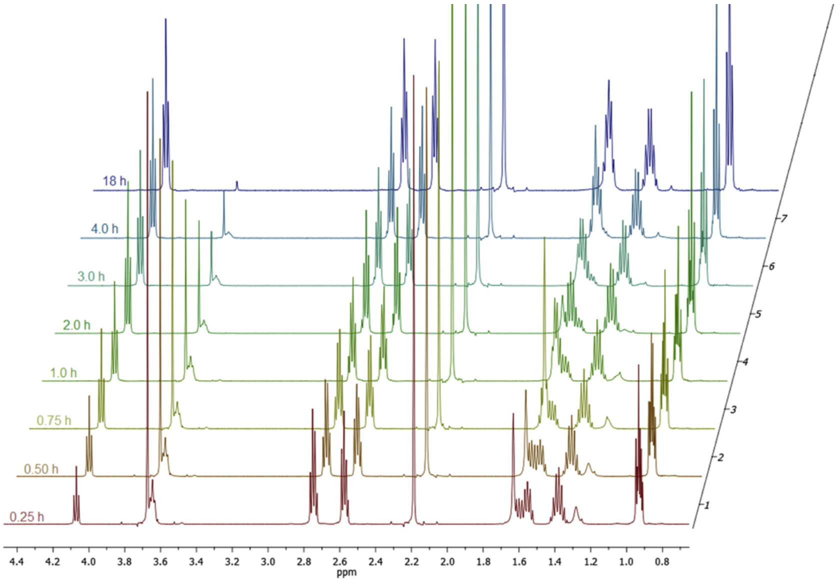
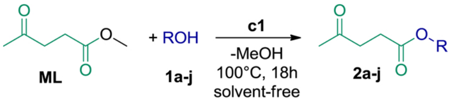
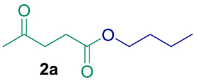
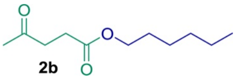
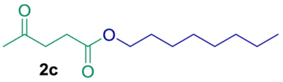
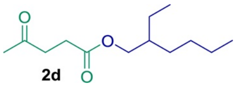
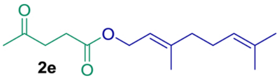
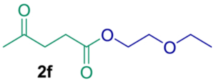
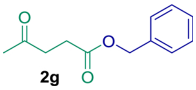
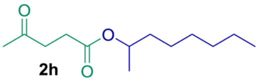
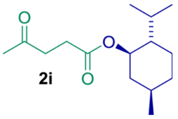
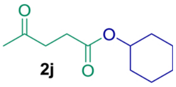


Fig. 4. ^{1}H NMR spectra of the reaction mixture over time in the conditions of entry 4.

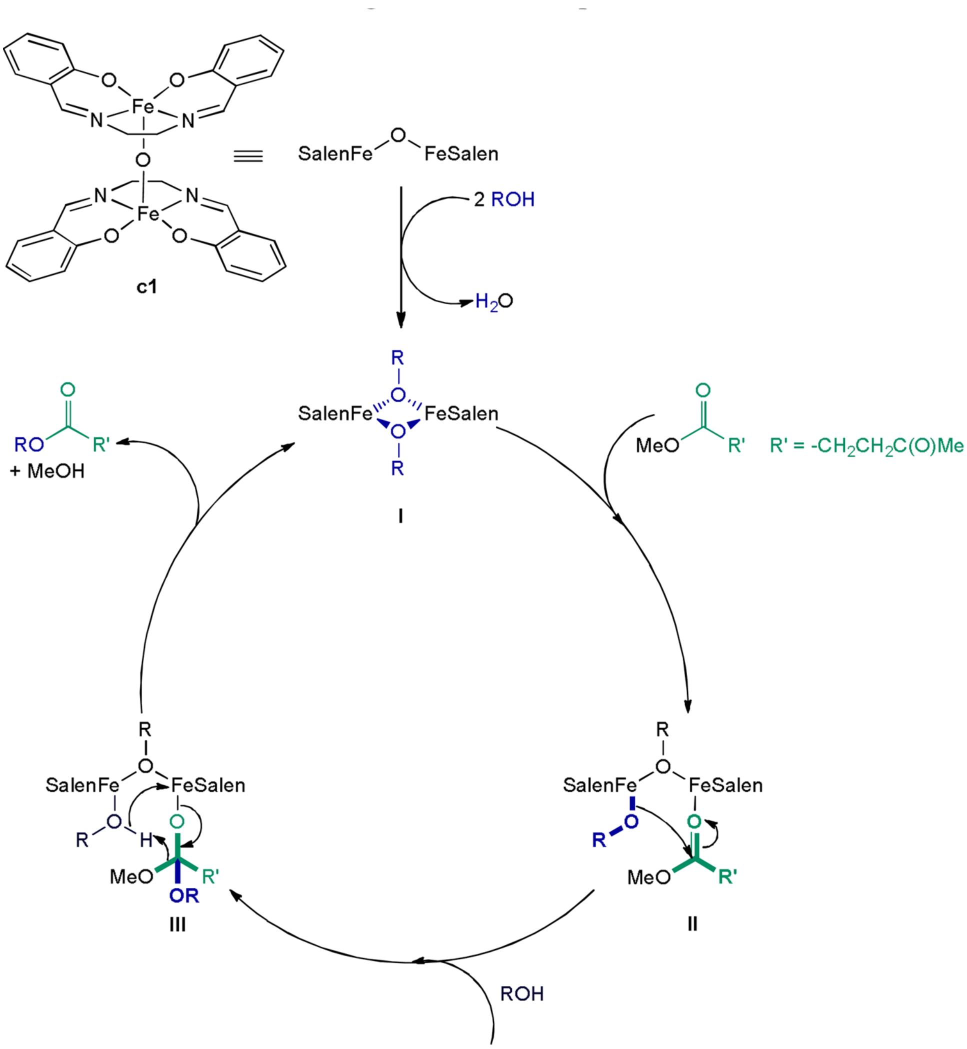
Table 4

Transesterification of methyl levulinate with alcohols.



Entry	Product	Use	Yield,[a] % (cat. loading 0.05% mol/mol)	Yield,[a] % (cat. loading 0.5% mol/mol)
1	 2a	Green plasticizer [23]; fuel additive [24].	95 ± 1	97 ± 1
2	 2b	Fuel additive [25].	95 ± 1	> 99
3	 2c	Cosmetics [26]	> 99	> 99
4	 2d	Green plasticizer [23]; cosmetics [26].	> 99	> 99
5	 2e	Coating [27].	67 ± 1	95 ± 1
6	 2f	Fuel additive [3].	85 ± 1	95 ± 1
7	 2g	Fuel additive [25].	81 ± 1	97 ± 1
8	 2h	–	56 ± 2	85 ± 1
9	 2i	Cosmetics [28].	22 ± 2	98 ± 1
10	 2j	–	38 ± 2	91 ± 2

[a] ^{1}H NMR yield; ratio ROH : MLA = 1.5 : 1; T = 100 °C.



Scheme 2. Proposed mechanism for the transesterification of methyl levulinate MLA.

To validate the presence of intermediates of type **I**, dimer **c1** was heated in *n*-butanol for 2 h. Removal of the solvent returned an orange solid, and its IR spectrum in nujol showed a clear shift of the band attributed to the asymmetric Fe-O-Fe stretching compared to that of **c1** (824 cm^{-1} vs 815 cm^{-1}). This evidence suggests the effective formation of the proposed species.

Finally, to disclose the identity of the catalyst at the end of the reaction, diethyl ether was added to the reaction mixture described by entry 1 of Table 3 (0.5 % mol/mol) with consequent precipitation of a brown solid. Its IR spectrum confirmed the presence of the dimeric species of type **I**, and therefore the same powder was reused to prove the persistence of activity: in the second run, performed at loading of 0.05 % mol/mol, the yield of *n*-butyl levulinate was 93 %, which indicates that the complex is still active and may be re-used.

2.3. Esterification of levulinic acid (LA)

Aiming to verify the flexibility of catalyst **c1**, we also attempted the esterification of levulinic acid with primary alcohols. Since in esterification [29] the intrinsic acidity of the substrate already provides a contribution of Brønsted acid catalysis, it is expected that conversions are already substantial without any added catalyst, and the introduction of a Lewis acid is intended to give further impulse to the reaction [29].

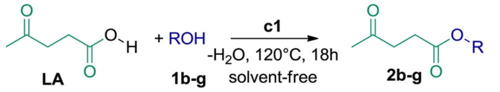
The reactions were performed under convenient conditions and with a dedicated setup to allow the progressive subtraction of water: the reaction temperature was set at 120 °C and the vessel was equipped with a short column of molecular sieves [19g] in order to trap the water and shift the equilibrium towards the products. The catalytic runs are reported in Table 5.

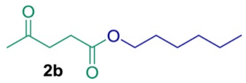
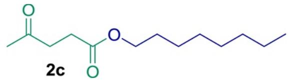
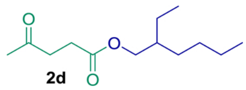
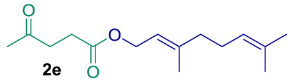
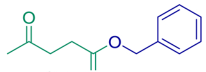
According to the premise, yields were already considerable without catalyst, and its presence served to sustain the reaction when its progression reduced the Brønsted acidity of the system. For example, the yield improved from 74 to 95 % with *n*-octanol (entry 2). It should be emphasized that this information is usually not mentioned in the catalytic reports of Table 2, which therefore do not clarify the contribution of the added catalyst to the yield.

A comparison between Tables 2 and 5 discloses that this homogeneous solvent-free system is competitive with literature results: the loading of catalyst is generally smaller, and a convenient ROH: LA can be adopted. Thus, *n*-hexyl, *n*-octyl and benzyl levulinate **2b**, **2c** and **2g** were obtained in yields comparable to those reported so far, while esterification with 2-ethylhexanol and geraniol to produce **2d** and **2e** are described for the first time in this paper.

These results disclose that complex **c1** displays significant Lewis activity also in esterification. This is also confirmed by the comparison with rare examples of literature [30] which describe the use of homogeneous iron(III) catalysts for esterification in less favorable reaction conditions (refluxing xylene, up to 30 h).

Table 5
Esterification of levulinic acid with alcohols.



Entry	Product	Yield,[a] % (no catalyst)	Yield,[a] % (cat. loading 0.5% mol/mol)
1	 **2b**	70 ± 1	80 ± 1
2	 **2c**	74 ± 1	95 ± 1
3	 **2d**	78 ± 1	95 ± 1
4	 **2e**	63 ± 1	87 ± 1
5	 **2g**	58 ± 1	82 ± 1

[a] ^1H NMR yield; ratio ROH : **LA** = 1.5 : 1; T = 120 °C; reaction time = 18 h.

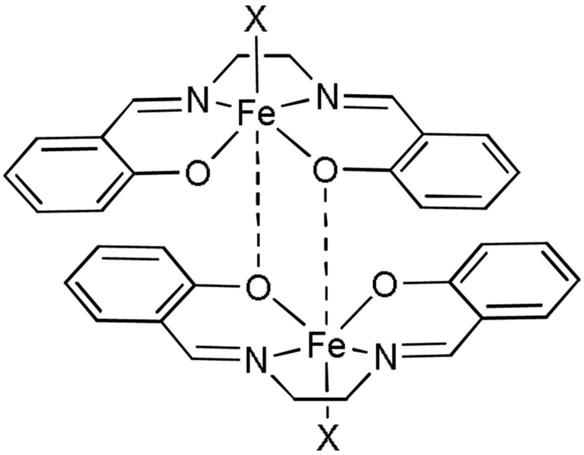


Fig. 5. Dimeric association found in the solid state for [Fe(Salen)(X)] complexes (X = Cl– or RCO_2–).

2.4. Proposed catalytic cycle for esterification

It is known that carboxylic acids RCO_2H transform dimer **c1** into the corresponding carboxylate [Fe(Salen)(RCO_2)] [31]. These species were studied in the solid state where a dimeric association was postulated, similar to what found for the chloro-derivative **c2** (Fig. 5).

However, it is reasonable that the corresponding monomeric species **c3** (Scheme 3) are instead present in solution, exactly as observed for the same **c2** [32]. Therefore, a likely [33] mechanism of esterification involves initial protonation of **c3** (Scheme 3), and upon coordination to the iron center (**I'**), the carbonyl group of levulinic acid is activated towards the nucleophilic attack of the alcohol. The intermediate oxonium species **II'** eliminates the product and water, leaving the metal ion ready to activate another molecule of substrate.

3. Conclusions

This work is part of the flourishing research aimed at the preparation of innovative bio-based products through valorization of levulinic acid. It is demonstrated the ability of a simple dimeric iron(III) complex to catalyze the homogeneous transesterification of methyl levulinate and the esterification of levulinic acid without solvents and at low catalyst loadings. As far as we know, this is the first systematic study based on a homogeneous catalytic system for these transformations, which have been so far a prerogative of heterogeneous catalysis. Therefore, the ensemble of results represents a significant extension in this emerging sector of biomass transformation, and demonstrates the emerging role of iron complexes in homogeneous catalysis under friendly conditions [34].

4. Experimental section

4.1. General

Reagents and solvents were purchased from Sigma-Aldrich. Known compounds were characterized comparing to the NMR spectra with those present in literature. These and all the new compounds have been characterized with a Bruker Avance Ultrashield 400 operating at proton frequency of 400 MHz of with a Varian 500 Oxford at proton frequency of 500 MHz. The following abbreviations were used for describing NMR multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; hept, heptet; m, multiplet; dd, doublet of doublets; dt, doublet of triplets; heptd, heptet of doublets; td, triplet of doublets; tt, triplet of triplets. Complexes **c1** and **c2** were prepared according to literature methods. [35]

4.2. Transesterification catalytic runs

Methyl levulinate (1.30 g, 10.0 mmol) and the appropriate amount of iron(III) catalyst, according to Tables 3, 4, were mixed in a round bottom flask. The alcohol was added in one portion in the desired amount, according to Tables 3, 4. The flask, connected to a cold trap, was heated in an oil bath at 100 °C under magnetic stirring. After 18 h, the cooled reaction mixture was analyzed by ^1H NMR spectroscopy. One run was performed on larger scale aiming at isolating the product. A mixture containing methyl levulinate (6.50 g, 50.0 mmol), *n*-butyl alcohol (5.55 g, 75.0 mmol) and **c1** (0.016 g, 0.025 mmol) was stirred 18 h at 100 °C. The mixture was filtered on a thin layer of Florisil, which was extracted with ethyl acetate (2 mL). The product was isolated after removal of the solvent under vacuum (7.3 g, 85 %).

4.3. Preparation of intermediate I

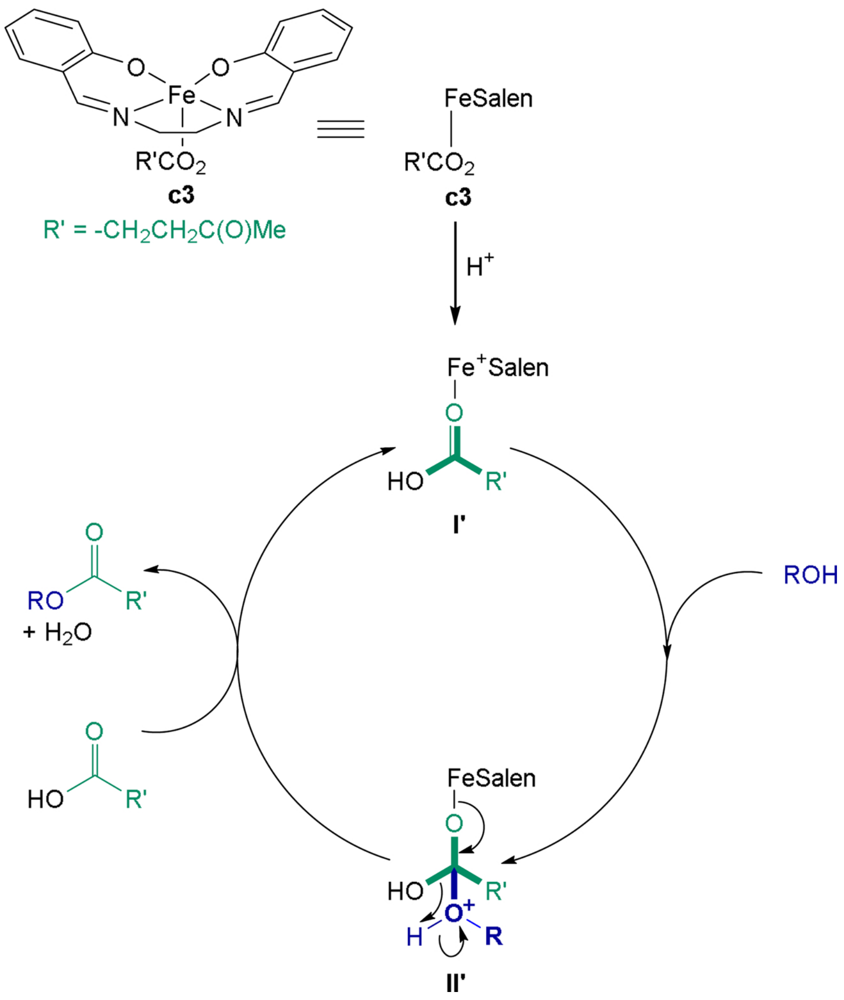
The iron(III) catalyst **c1** (0.033 g, 0.050 mmol) and *n*-butanol (11.1 g, 150 mmol) were mixed in a round bottom flask. The flask, connected to a cold trap, was heated in an oil bath at 100 °C under magnetic stirring for 2 h. Then the alcohol was removed under vacuum and an orange powder was obtained. Selected IR signals (nujol, ν) = 1654, 1629, 1598, 1541, 906, 861, 824 cm^{-1}.

4.4. Catalyst recover and recycle

Methyl levulinate (1.30 g, 10.0 mmol) and the iron(III) catalyst **c1** (0.033 g, 0.050 mmol) were mixed in a round bottom flask. The alcohol *n*-butanol (0.556 g, 7.50 mmol) was added in one portion. The flask, connected to a cold trap, was heated in an oil bath at 100 °C under magnetic stirring. After 18 h the reaction was cooled, and diethyl ether was added. A brown solid precipitated, which was recovered by centrifugation. The solid was identified as the intermediate **I**, and was reused for a second catalytic run at a loading of 0.050 % mol/mol. The yield of product was 93 %.

4.5. Esterification catalytic runs

Levulinic acid (0.580 g, 5.00 mmol) and the iron(III) catalyst **c1** (0.016 g, 0.025 mmol) were mixed in a round bottom flask. The alcohol



Scheme 3. Proposed mechanism for the esterification of levulinic acid **LA**.

was added in one portion (7.50 mmol). The flask, equipped with a short column of molecular sieves, was heated in an oil bath at 120 °C under magnetic stirring. After the catalytic runs, the cooled reaction mixture was analyzed by ^{1}H NMR spectroscopy.

^{1}H NMR data (500 MHz, $CDCl_3$, δ)= **2a**: 4.07 (t, J =6.7 Hz, 2 H), 2.74 (t, J =6.6 Hz, 2 H), 2.57 (t, J =6.6 Hz, 2 H), 2.19 (s, 3 H), 1.66 – 1.54 (m, 2 H), 1.43 – 1.31 (m, 2 H), 0.92 (t, J =7.4 Hz, 3 H); **2b**: 4.06 (t, J =6.8 Hz, 2 H), 2.74 (t, J =6.4 Hz, 2 H), 2.57 (t, J = 6.5, 2 H), 2.19 (s, 3 H), 1.67 – 1.57 (m, 2 H), 1.39 – 1.22 (m, 6 H), 0.88 (t, J =6.9 Hz, 3 H); **2c**: 4.06 (t, J =6.8 Hz, 2 H), 2.75 (t, J =6.6 Hz, 2 H), 2.57 (t, J =6.6 Hz, 2 H), 2.20 (d, J =5.0 Hz, 3 H), 1.74 – 1.50 (m, 2 H), 1.40 – 1.08 (m, 10 H), 0.88 (t, J =6.8 Hz, 3 H); **2d**: 4.11 – 3.92 (m, 2 H), 2.78 (t, J =6.6 Hz, 2 H), 2.61 (t, J =6.6 Hz, 2 H), 2.22 (s, 3 H), 1.59 (m, 1 H), 1.48 – 1.14 (m, 8 H), 1.00 – 0.84 (m, 6 H); **2e**: 5.33 (t, J =6.5 Hz, 1 H), 5.08 (t, J =6.7 Hz, 1 H), 4.59 (d, J =7.1 Hz, 2 H), 2.75 (t, J =5.7 Hz, 2 H), 2.58 (t, J =6.6 Hz, 2 H), 2.19 (s, 3 H), 2.14 – 2.07 (m, 2 H), 2.07 – 2.00 (m, 2 H), 1.69 (s, 3 H), 1.68 (s, 3 H), 1.60 (s, 3 H); **2f**: 4.22 (t, J =4.7 Hz, $-OCH_2CH_2OCO$-, 2 H), 3.62 (t, J =4.7 Hz, -OCH_2CH_2OCO-, 2 H), 3.53 (q, J =7.2 Hz, CH_3CH_2O-, 2 H), 2.75 (t, J =6.5 Hz, $CH_3COCH_2CH_2OCO$-, 2 H), 2.61 (t, J =6.6 Hz, $CH_3COCH_2CH_2OCO$-, 2 H), 2.19 (s, $-COCH_3$, 3 H), 1.21 (t, J =7.0 Hz, CH_3CH_2O-, 3 H); **2 g**: 7.39 – 7.27 (m, Ph-, 5 H), 5.12 (s, $PhCH_2O$- 2 H), 2.77 (t, J =6.4 Hz, $CH_3COCH_2CH_2OCO$-, 2 H), 2.63 (t, J =6.5 Hz, $CH_3COCH_2CH_2OCO$-, 2 H), 2.19 (s, $-COCH_3$, 3 H); **2h**: 4.93 – 4.83 (m, 1 H), 2.74 (t, J =6.5 Hz, 2 H), 2.55 (t, J =6.3 Hz, 2 H), 2.19 (s, 3 H), 1.58 – 1.42 (m, 2 H), 1.35 – 1.22 (m, 8 H), 1.19 (d, J =4.9 Hz, 3 H), 0.86 (t, J =6.9 Hz, 3 H); **2i**: 4.67 (td, J = 10.9, 4.3 Hz, 1 H), 2.74 (t, J =6.6 Hz, 2 H), 2.55 (t, J =6.8 Hz, 2 H), 2.19 (s, 3 H), 2.02 – 1.92 (m, 1 H), 1.86 (dhept, J = 7.0, 2.8 Hz, 1 H), 1.73 – 1.64 (m, 2 H), 1.52 – 1.41 (m, 1 H), 1.41 – 1.32 (m, 1 H), 1.08 – 0.94 (m, 2 H), 0.89 (dd, J = 6.8, 1.3 Hz, 6 H), 0.87 – 0.83 (m, 1 H), 0.75 (d, J =7.0 Hz, 3 H); **2j**: δ 4.80 – 4.68 (m, 1 H), 2.74 (t, J =6.6 Hz, 2 H), 2.55 (t, J =6.6 Hz, 2 H), 2.19 (s, 3 H), 1.86 – 1.79 (m, 2 H), 1.74 – 1.65 (m, 2 H), 1.58 – 1.47 (m, 1 H), 1.45 – 1.22 (m, 5 H).

Declaration of Competing Interest

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

CRediT authorship contribution statement

Massimo Melchiorre: Investigation, Validation. **Raffaele Amendola:** Investigation. **Vincenzo Benessere:** Validation, Visualization. **Maria E. Cucciolito:** Conceptualization, Writing - original draft. **Francesco Ruffo:** Supervision. **Roberto Esposito:** Conceptualization, Writing - original draft.

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