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Sn(II)-catalyzed β-citronellol esterification: a Brønsted acid-free process for synthesis of fragrances at room temperature

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Simple $SnCl_2 \cdot 2H_2O$ was demonstrated to be able to catalyze β-citronellol esterification with acetic acid at room temperature under solvent-free conditions, achieving high conversion and ester selectivity (*ca*. 88 and 99 %, respectively). Tin (II) chloride is a stable and water tolerant Lewis acid, commercially available and lesser corrosive than Brønsted acid catalysts. This selective process is an attractive alternative to the mineral acid-catalyzed process because avoid products neutralization common in those reactions. Effects of main reaction parameters such as reactants stoichiometry, temperature, solvent, and catalyst concentration were assessed. Among tin catalysts evaluated, $SnCl_2$ was the most active and selective. Moreover, $SnCl_2$ was as active as sulfuric and *p*-toluenesulfonic acid catalysts, Brønsted acids investigated herein, with addition advantages of being a solid and less corrosive catalyst.

Introduction

β-Citronellol is the acyclic terpenic alcohol extensively used and is a valuable raw material for the industries of perfumes, beverage, food, and pharmaceuticals [1-3]. β-citronellyl acetate is an important flavor ingredient and fragrance being industrially produced by enzymatic processes or via Brønsted acid-catalyzed reactions [4,5]. Indeed, the synthesis of citronellyl acetate could be even more attractive when carried out via environmentally benign processes, under solvent-free conditions and where steps of products neutralization are avoided and the catalyst recovery facilitate, minimizing the generation of salts and effluents [6].

Among catalysts employed in esterification reactions, Lewis acids have significant advantages compared to the liquid Brønsted acid catalysts, such as its low corrosiveness and great water tolerance [7,8]. On the other hand, enzymatic catalysts commonly used in esterification are expensive and require rigid control of temperature and acidity of reaction medium. Actually, enzymatic catalysts have been intensively used in the terpenic alcohol esterification, however, their high cost and the difficulty of catalyst recovery are negative aspects of these processes, that compromised their application in a large scale [9,10]. On this regard, tin (II) chloride is an inexpensive and easily handling solid catalyst that could be more potentially active in the acid-catalyzed reactions [11-15].

The development of selective processes to functionalize monoterpenes based on commercial and simple metal catalysts is a goal that has been pursued by our research group [16,17]. Recently, tin (II) halide catalysts were successfully tested in the ketalization and esterification reactions of fatty acids and glycerol [18,19]. Earlier, tin catalysts were successfully used in transesterification reactions of vegetal oil [20]. Nevertheless, any work describing its use in the terpenic alcohols esterification until this moment. Herein, we wish describe a simple and efficient Sn(II)-catalyzed β-citronellol esterification process with HOAc in the absence of solvent and at room temperature. We paid special attention to assess factors driving esterification selectivity and to optimizing the reaction conditions. Remarkably, at room temperature the $SnCl_2$ catalyst promoted esterification of β citronellol with HOAc achieved a very high selectivity (*ca*. 99 %) with *ca*. 88 % of conversion, within shorter reaction time than those reported in the literature [21,22]. To the best of our knowledge, this is the first report of terpenic alcohol esterification reaction catalyzed by $SnCl_2$.

Thus, the present study describes using of $SnCl_2$ as catalyst under mild reaction conditions (*ca*. temperature and pressure room) in the β citronellyl acetate synthesis in absence of solvent. Herein, we investigated effects of main reaction parameters in the conversion and selectivity, in addition to compare the catalytic activity of Lewis or Brønsted acids.

Experimental

Chemicals

All chemicals are commercially available and utilized without prior handling. $SnCl_2 \cdot 2H_2O$ (95 % wt.), SnF_2, $SnBr_2$ and $Sn(CH_3COO)_2$ (99 % wt), were purchase from Sigma Aldrich. Brønsted acid catalysts, H_2SO_4 (98% wt.) and *p*-toluenesulfonic acid (99 % wt.) were acquired from Aldrich and Proquimios, respectively. β-citronellol (99 % wt.), was purchased from Sigma-Aldrich and used without as received.

Catalytic runs

Catalytic runs were performed in a glass reactor (50 mL) equipped with a magnetic stirrer and sampling septum. Typically, β-citronellol and HOAc were dissolved in an adequate molar ratio (15 mL solution), and then the reaction was initiated by the adding of Sn(II) catalyst (*ca*. 1 to 10 mol %).

Reaction progress was followed by GC analyses of aliquots taken at regular time intervals in a Shimadzu GC 2010 instrument, FID, fitted with Carbowax 20M capillary column. Toluene was the internal standard. To calculate the reaction conversions, were compared the corresponding product chromatographic peak areas with the calibrating curves. To adjust the concentration to the calibration curve we diluted all the aliquots with acetonitrile.

Products identification

The reaction products were analyzed on a Shimadzu MS-QP 2010 ultra mass spectrometer instrument operating at 70 eV, coupled with a Shimadzu 2010 GC. We isolated major product by column chromatography using silica gel (60G). The ^1H and ^{13}C NMR spectra was recorded on the Mercury-300 Varian Spectrometer at 300 and 75 MHz respectively, in $CDCl_3$ solution using TMS as internal standard. FT-IR spectroscopy analyses carried out in Varian 660 FT-IR Spectrometer. The spectroscopic data of the β-citronellyl acetate (**Fig. 1**) are summarized as follow:
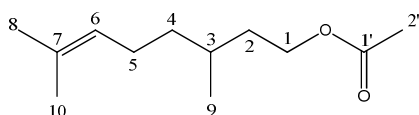

Fig.1. β-citronellyl acetate

^1H NMR (300 MHz, $CDCl_3$-*d1*): δ (integration, multiplicity, coupling constant, attribution); 0.90 (d, 3H, 9 – C$\underline{H}_3$); 1.13 – 1.53 (m, 5H, 2 – C$\underline{H}_2$, 3 – C$\underline{H}$ and 4 – C$\underline{H}_2$); 1.60 (s, 3H, 10 – CH_3); 1.68 (s, 3H, 8 – CH_3); 1.92 – 2.04 (m, 2H, 5 – CH_2); 2.04 (s, 3H, 2' – OCCH_3); 4.06 – 4.12 (m, 2H, 1 – OCH_2); 5.05 – 5.10 (m, 1H, 6 – CH).

^{13}C NMR (75 MHz, $CDCl_3$-*d1*): δ (integration, multiplicity, coupling constant, attribution); 17.63 (C10); 19.38 (C2'); 21.05 (C9); 25.35 (C5); 25.71 (C8); 29.42 (C3); 32.37 (C2); 36.94 (C4); 63.02 (C1); 124.52 (C6); 131.34 (C7); 171.26 (C1').

(FT-IR) ν(cm^{-1}): 2962; 2922; 1743; 1455; 1367; 1239; 1055.

GC-MS (m/z/ relative intensity): 198/0.05; 138/23; 123/31; 109/17; 95/57; 81/77; 69/69; 55/42; 41/100.

Results and discussion

General aspects

Recently, we described the use of tin halides as catalysts in the esterification reactions of glycerol as well as free fatty acids [17,18]. In those works, among tin catalysts assessed, $SnCl_2$ was always the most effective catalyst. Thus, inspired by these findings, we investigate the catalytic activity of $SnCl_2 \cdot 2H_2O$ in the terpenic alcohols esterification reactions. β-citronellol was selected as model molecule and initially the reactions were carried out in CH_3CN solutions.

Effect of temperature in the $SnCl_2$-catalyzed β-citronellol esterification with HOAc

The $SnCl_2$-catalyzed β-citronellol esterification with HOAc was accomplished at different temperatures (*ca*. 298 to 333 K) in

presence or absence of catalyst; by simplification, only the main results are displayed in Table 1.

Despites the acidity of HOAc, and even using a slight excess them in relation to β-citronellol (i.e. molar ratio of 2:1), any ester formation was detected in absence of catalyst, regardless reaction temperature studied (i.e. 298 or 333 K, Table 1).

On the other hand, in presence of $SnCl_2$ the β-citronellol esterification reactions became catalytic at room temperature or when the reaction it were heated to 333 K (Runs 3, 4, Table 1).

Table 1. Temperature effects in the $SnCl_2$-catalyzed β-citronellol esterification with HOAc[a]

Run	T (K)	$SnCl_2$ (mol %)	Convers. (%)	Selectivity (%)		
				1	Ni	olig.
1	298		0	0	0	0
2	333	0	0	0	0	0
3	298	10	42	90	2	8
4	333	10	21	40	2	58

[a]Reaction conditions: β-citronellol (7.8 mmol), HOAc (15.6 mmol), CH_3CN solution (15 mL), 6 h. [b](1) = β-citronellyl acetate; ni = complex mixture of non-identified products.

We verified that an increase of temperature affected the conversion and reaction selectivity. Noticeably, the undesirable formation of oligomers (ca. 58 % selectivity, Table 1) in the reactions performed at 333 K compromised the ester selectivity. Conversely, oligomers were not formed when the reaction was carried out at 298 K. Oligomers are not detectable by GC analysis because high molar weight. However, a checking of mass balance proven that oligomers were formed, comparing GC peaks area of formed products against GC peak area of β-citronellol consumed. In addition, after reaction solution cooling the oligomers were precipitated as a white solid and analyzed by FT-IR spectroscopy, who allow its identification.
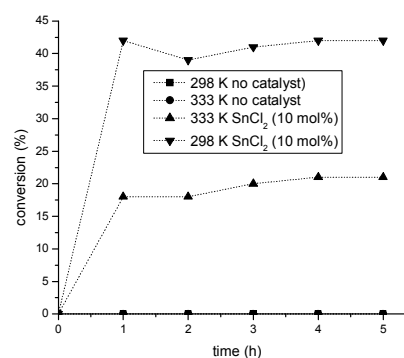

Fig. 2. Effects of temperature on $SnCl_2$-catalyzed β-citronellol esterification[a]

[a]Reaction conditions: β-citronellol (7.8 mmol), HOAc (15.6 mmol), CH_3CN solution (15 mL), 6 h.

The increase of the conversion rate with the decreasing of temperature suggest an exothermal character for this process (**Fig. 2**). Although this aspect was not been further described in literature, it was described another kind of reaction involving alcohols and

carbonylic reactant (i.e. glycerol and ketone), and the same observation was find out [23].

Thermodynamic studies

To calculate the equilibrium constant for the β-citronellol esterification reaction with HOAc (K_{eq}) some considerations deserves be highlighted. Firstly, it should be considered that it is independent of HOAc concentration (due to its excess). In addition, we must take into account that the reaction products (i.e. water and β-citronellyl acetate) are formed with the same concentration. Thus, after these simplifications, we can write the equation for equilibrium constant as follow:

$$K_{eq} = [\text{β-citronellyl acetate}]^2/[\text{β-citronellol}]$$
Equation 1

The initial concentration of β-citronellol was equal to 0.873 mol L^{-1}. Table 2 shows the equilibrium constants for each reaction at the different temperatures studied. The Equation 2 is true when the enthalpy variation is constant with temperature.

$$\ln K_{eq} = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$

Equation 2

Table 2. Values of enthalpy and entropy variation for the SnCl$_2$-catalyzed β-citronellol esterification reactions with HOAc

Temperature (K)	Equilibrium constant (Keq)	-RlnKeq	ΔH (kJ mol^{-1})	ΔS (kJ mol^{-1})
298	0.161	0.150		
308	0.113	0.178		
318	0.073	0.215	-0.312	0.0012
328	0.046	0.252		

[a]Reaction conditions: β-citronellol (7.8 mmol), HOAc (15.6 mmol), CH$_3$CN solution (15 mL), 6 h.

From data shown in Table 2, we could build the linear plots of ln K_{eq} versus ln 1/T (**Fig. 3**) and by using the Equation 2 the respective values of ΔS and ΔH were calculated.

Whilst the slope of the curve give the value of ΔH and the Y axis intercept provide ΔS. The values for enthalpy and entropy variations were found to be equal to -0.312 kJ mol^{-1} and 0.0012 kJ mol^{-1}, respectively (**Fig.3**).

The negative value ΔH confirm the exothermic character of reaction, that explain the increased observed in conversion when the temperature was decreased of 333 to 298 K (**Fig.2**).
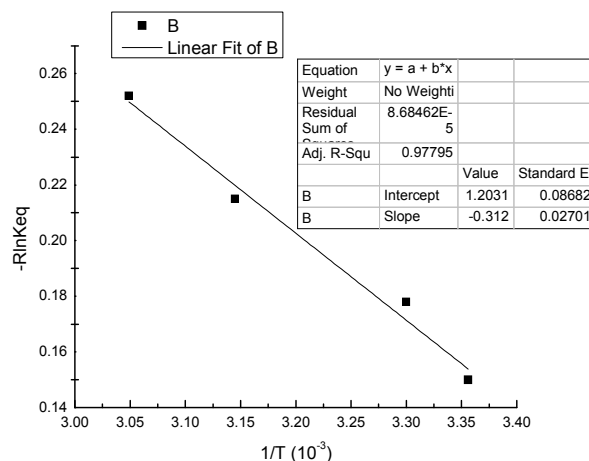

Fig. 3. Linear plot –RlnKeq versus 1/T

Effect of reactants molar ratio in the SnCl$_2$-catalyzed β-citronellol esterification

When performed at room temperature, the only product obtained in the β-citronellol esterification with HOAc was β-citronellyl acetate (**Fig.4**), always with selectivity equal or higher than 95 %, determined via GC-MS analyses.
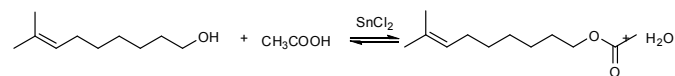

Fig. 4. SnCl$_2$.catalyzed β-citronellol esterification with HOAc[a]

[a]Reaction conditions: β-citronelol:HOAc proportion 1: 2; SnCl$_2$ (10 mol %); 298 K; 6 h.

The reactants stoichiometry is a key aspect in this reaction and its effect was investigated in the range of 1:1 to 1:10 (Table 3). Although the β-citronellol:HOAc molar ratio has been increased to 1:10, only a poor conversion (*ca*. lower than 5 %) was reached in catalyst absence. Conversely, in the SnCl$_2$-catalyzed reactions the conversion drop to almost 90 % when the proportion of reactants was equal or higher than 1: 6. Any decreasing of ester selectivity was observed in all these reactions at room temperature. Selectivity of β-citronellyl acetate remained equal or higher than 95 % independently of reactants molar ratio employed**.**

The kinetic curves displayed in **Fig. 5** show that both initial rate and final conversion were almost the same in the reactions with molar ratio between 1:6 and 1:10. Thus, this was the proportion selected to perform the reactions in absence of solvent. We verified that without solvent and with molar ratio equal to 1:6, the reaction behavior was the same in terms of conversion and selectivity (not showed in Figure 4 by simplification).

In addition to the recovery problems and toxicity, some enzymatic catalysts are sensible to acetic acid presence, that become the choice of the adequate solvent an crucial aspect for those reactions [24.25].

However, in the SnCl$_2$-catalyzed reaction described herein, the reactants themselves were used as liquid phase and thus this problem

was easily circumvented.

Table 3. Effect of reactants stoichiometry in the SnCl$_2$-catalyzed β-citronellol esterification with HOAc[a,b]

Run	HOAc: β-citronelol molar ratios	Conversions (%)	
		SnCl$_2$-catalyzed reactions	Blank-reactions
1	2:1	43	0
2	4:1	69	0
3	6:1	88	0
4	8:1	89	<5
5	10:1	89	5

[a]Reaction conditions: β-citronellol (7.8 mmol), CH$_3$CN solution (15 mL), SnCl$_2$ (10 mol %), 298 K, 3 h. [b]β-citronellyl acetate selectivity determined via GC was equal or higher than 95 % in all catalytic runs.
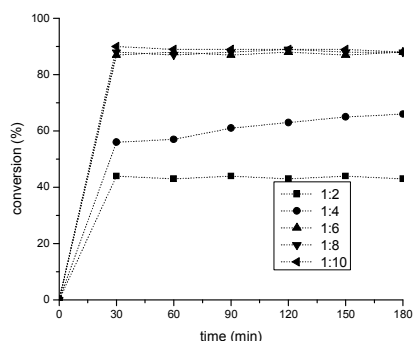

Fig. 5. Kinetic curves of SnCl$_2$-catalyzed β-citronellol esterification with HOAc using different molar ratios between reactants.

[a]Reaction conditions: β-citronellol (7.8 mmol), SnCl$_2$ (10 mol %) 3 h.

The reason of the fast deactivation of catalyst was investogated. We performed experiments using different initial concentrations of water (ca. 0.1 to 10 mol % in relation to the catalyst). We verified that beginning reactions with water concentration higher than 10 mol % resulted in a noticeable decreased of the initial rate. Starting a reaction with 1:6 molar ratio of β-citronellol: HOAc and an initial amount of water equal to 10 mol %, resulted in the lowering conversion rate after 30 minutes for 40 %. Contrarily, in the reactions in absence of water, conversions near to 90 % were obtained (**Fig. 5**). Besides to shift equilibrium toward reactants, water may coordinate to the tin(II) cations, compromising its activity.

Effect of catalyst concentration in the SnCl$_2$-catalyzed β-itronellol esterification

In all runs catalyzed by Sn(II), the high initial rate of β-citronellol esterification allows to reach a maximum conversion within first thirty minutes of reaction, staying almost constant from this point forward regardless catalyst concentration (Figure 5)
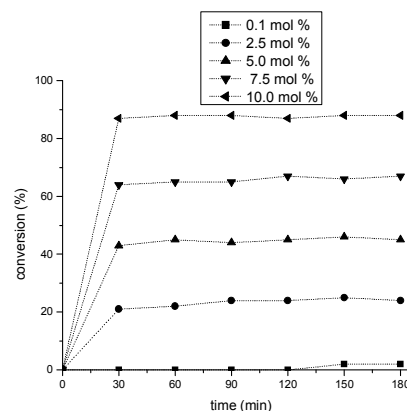

Fig. 6. Effect of SnCl$_2$.2H$_2$O concentration in the β-citronellol esterification with HOAc.[a]

[a]Reaction conditions: β-citronellol (13.1 mmol), HOAc (78.6 mmol), 298 K, 3 h.

From rate constant measured within first thirty minutes of reaction (i.e. mmol β-citronellol converted/ 1800 s) for each run with a specific catalyst concentration (*ca*. 0.10 to 10 mol %) it was possible to build linear plot (**Fig.6**) and determine the reaction order in relation to the SnCl$_2$ concentration.

A high linear coefficient (R^2 = 99.9 %) clearly show that a first order dependence in relation to SnCl$_2$ concentration determined by slope of curve (*ca*. 1.2) may be suggested for these reactions (**Fig.7**).
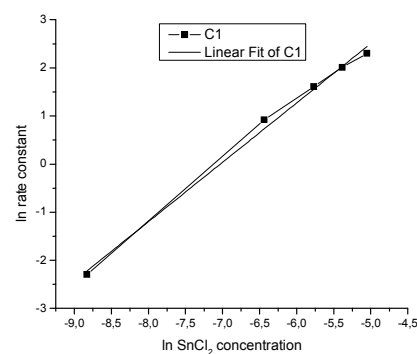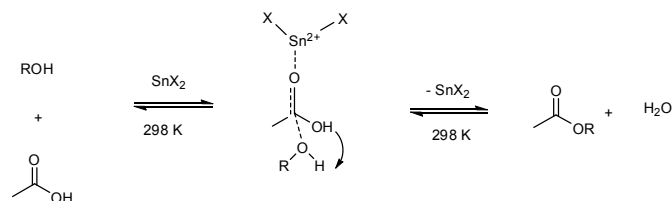

Fig. 7. Determination of order in relation to the SnCl$_2$ catalyst concentration

A first order dependence have been also verified in SnCl$_2$-catalyzed reaction, in which the substrates were glycerol and HOAc [26]. Thus, it is suggestive that in the determining step of reaction rate only one tin atom should be involved (Scheme 1).

Scheme 1. Mechanism proposal of tin-catalyzed esterification of alcohols with HOAc

Although there are different approaches in literature on regards of carbonyl group activation could be made by tin coordinated to the anionic ligands or partially dissociated, it is reasonable suppose that the carbonyl polarization become more favorable its attack by hydroxyl group as described in the Scheme 1 [27].

Table 4. Effect of $SnCl_2.2H_2O$ concentration in the β-citronellol esterification with HOAc[a]

Run	$SnCl_2$ (mol %)	Conversion (%)	Product selectivity (%)		
			1	Ni	Olig
1	0.1	2	99	1	0
2	2.5	21	96	4	0
3	5.0	44	99	1	0
4	7.5	64	97	3	0
5	10.0	87	99	1	0

[a]Reaction conditions: β-citronellol (13.1 mmol), HOAc (78.6 mmol), 298 K, 3 h. [b](1) = β-citronellyl acetate; ni = complex mixture of non-identified products.

It can be noted that decreasing of the catalyst concentration does not result in any significant change on the reaction selectivity. Regardless of $SnCl_2$ concentration, the β-citronellyl acetate selectivity **(1)** remained higher than 96 % and with no oligomers formation (Table 4). A highly selective conversion of β-citronellol to β-citronellyl acetate was achieved using $SnCl_2$ at 10 mol % within reaction time shorter than those reported by the literature in enzymatic processes [28]. Those authors suggested that HOAc had an inhibitory effect on catalytic action of lipase assessed [29].

Lewis or Brønsted acid-catalyzed β-citronellol esterification with HOAc

The effect of catalyst nature (i.e. Brønsted or Lewis acids) was assessed in the kinetic curves obtained are displayed in **Fig. 8**. In the most of case, the acid strength is determining for the activity of Brønsted acid catalysts. If considered that sulfuric and p-toluenesulfonic acids were used at same hydrogenionic concentration, the fact of reactions catalyzed by them have achieved conversions almost equals (ca. 90%) could be attributed to probable levelling effect caused by the composition of reaction medium.
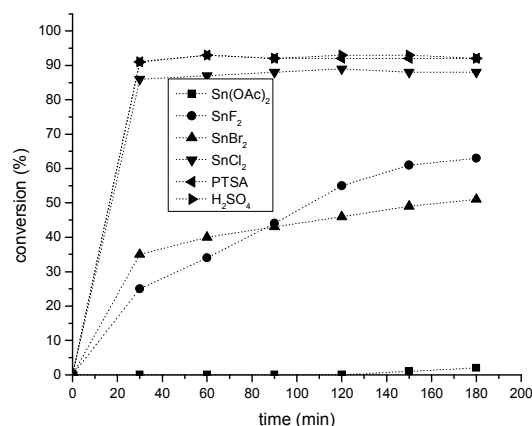

Fig. 8. Effect of catalyst nature in β-citronellol esterification with HOAc[a,b]

[a]Reaction conditions: β-citronellol (13.1 mmol), HOAc (78.6 mmol), Lewis acid catalyst (10 mol % of Sn^{2+} in relation to β-citronellol); Brønsted acid catalyst (10 mol % of H^+ in relation to β-citronellol), 3 h, 25 °C.

[b]Selectivity of β-citronellyl acetate was higher than 98% in all runs, except in the $Sn(OAc)_2$-catalyzed reaction where it does not obtained.

On the other hand, steric or electronic factors of anionic ligands may change the catalytic activity of Lewis acid such as Sn(II) salts. However, it was also important take in account the solubility of catalysts. $Sn(OAc)_2$ and $SnBr_2$ were partially soluble, whereas to $SnCl_2$ and SnF_2, who were completely solubilized. For these reason, tin acetate or bromide were the lesser active catalysts than the soluble salts. In addition, the lowest activity of $Sn(OAc)_2$ may be attributed to low lability of acetate ligand. This bidentate ligand probably hinder the activation of carbonyl group of HOAc by the few molecules of $Sn(OAc)_2$ soluble catalyst. In this sense, is reasonable accept that the activation of carbonyl group of HOAc depends on the Sn(II) cations concentration available in the solution.

Conversely, the highest activity of $SnCl_2$ may be attributed not only to its high solubility as well as to the higher stability of chloride anion, who is recognized as a leaving group better than fluoride anion present in the SnF_2. This result is in agreement with the literature [25].

Finally, the most auspicious result is the high activity of $SnCl_2$; although it has been slightly lower than Brønsted acids studied, the use of tin catalyst has significance handicaps such as to avoid neutralization steps, generate less corrosion and being easily handling because it is a solid compound.

Conclusions

An efficient process to synthesize terpenic esters (i.e. β-citronellyl acetate) was developed. Tin (II) chloride dihydrate, an inexpensive and commercially available catalyst was used in environmentally benign reaction conditions (i.e. in absence of solvent and at room temperature). Tin(II) chloride catalyst efficiently promoted the β-citronellol esterification reaching the same conversion and

selectivity (*ca*. 90 and 98 %, respectively) that corrosive Brønsted acid catalyst (i.e. H_2SO_4). In addition, among others tin catalysts assessed herein, we find out that $SnCl_2$ was most active and selective. The comparison with others tin catalyst provide the following order in terms of activity: $SnCl_2 > SnF_2 > SnBr_2 > Sn(OAc)_2$. Tin-catalyzed esterification processes are lesser corrosive than those catalyzed by Brønsted acids and faster and cheaper than enzimatic processes reported in the literature.

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Notes and references

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1 P Gallezot, *Catal. Today* 2007, **121**, 76.

2. C Chapuis, Jacoby D Jacoby *Appl Catal A* 2001*,* **221**, 93.

3. J. Muzart *Tetrahedron* 2003, **59**, 5789.

4. N. A. Serri, A. H. Kamaruddin, K. Y. T. Len, *Food Bioprod. Proces.* 2010, **88**, 327.

5. E. J. Lenardao, G. V. Botteselle, F. Azambuja, G. Perin, R. G. Jacob, *Tetrahedron* 2007, **63**, 6671.

6. P. T. Anastas, L. B. Bartlett, M. M. Kirchhoff, T. C. Williamson *Catal Today* 2000**, 55**, 11.

7. M. L..da Silva, A. P. Figueiredo, A. L. Cardoso, R. Natalino, M. J. da Silva, *J. Am. Oil Chem. Soc*. 2011, **88**, 1431.

8. A. L. Cardoso, S. C. G. Neves, M. J. da Silva, *Energ. Fuel* 2009, **23**, 1718.

9. H. F. Castro, E. B. Pereira, W. A. Anderson, *J. Braz. Chem. Soc*. 1996, **7**, 1.

10. F. Fonteyn, C. Blecker, G. Lognay, M. Marlier, M. Severin. *Biotechnol. Lett.* 1994, **16**, 693.

11. C. S. Cho, D. T. Kim, H.-J. Choi, T.-J. Kim, S. C. Shim, *Bull. Korean Chem. Soc.* 2002, **23**, 539.

12. Y. Hayashi, Y. Sasaki *Chem. Commun.* 2005, 2716.

13. A. Dutta, A.K. Patra, H. Uyama, A. Bhaumik *ACS Appl. Mat. Interf.* 2013, **5**, 9913.

14. N.T. Nguyen, K.J. Thurecht, S.M. Howdle, D.J. Irvine, Polym. Chem. 2014, **5**, 2997.

15. J. Luo, J. Yu, R.J. Gorte, E. Mahmoud, D.G. Vlachos, M.A. Smith *Catal. Sci. Technol.*, 2014, **4**, 3074.

16. M. J. da Silva, D. M. Carari DM *Catal. Lett.* 2014, **144**,:615.

17. M. J. da Silva, D. M. Carari *Catal. Lett*. 2012, **142**, 251.

18. F. L. Menezes, M. D. O. Guimaraes, M. J. da Silva, *Ind. Eng. Chem. Res.* 2013, **52**, 16709.

19. M. J. da Silva, C. E. Goncalves, L. O. Laier, *Catal. Lett.* 2011, **141**, 1111.

20. S. Einloft, T. Magalhaes, D. Aranda, J. Dullius, R. Ligabue, *Energ. Fuels*, 2008, **22**, 671.

21. K. P. Dhake, K. M. Deshmukh, Y. P. Patil, R. S. Singhal, B. M. Bhanage *J. Biotechnol.* 2011, **156**, 46.

22. H. Stamatis, P. Christakopoulos, D. Kekos, B. J. Macris, F. N. Kolisis *J. Mol. Catal. B*, 1998, **4**, 229.

23. M. R. Nanda, Z. Yuan, W. Qin, H. S. Ghaziaskar, M.-A. Poirier, C. C. Xu, *Fuel*, 2014, **117**, 470.

24. G. B. Oguntimein, W. A. Anderson, M. Moo-Young, *Biotechnol. Lett.* 1995, **17**, 77.

25. M. Karra-Chaabouni, S. Pulvin, D. Touraud, D. Thomas, *Biotechnol. Lett.* 1996, **18**, 1083.

26. A. B. Ferreira, A. L. Cardoso, M. J. da Silva, *Catal. Lett.* 2013, **143**, 1240.

27. L. Li, T. I. Korányi, B. F. Sels, P. P. Pescarmona, *Green Chem.* 2012, **14**, 1611.

28. P. Claon, C. Akoh, *Enzime Microb. Technol.* 1994, **16**, 835.

29. H. F. de Castro, P. C. de Oliveira, E. B. Pereira, *Biotechnol. Lett*. 1997, **19**, 229.