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Esterification of free fatty acids (Biodiesel) using nano sulfated-titania as catalyst in solvent-free conditions

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ABSTRACT

Nano sulfated titania was tested as catalyst for esterification of free fatty acids, specially methanolic and ethanolic esterification of stearic acid (biodiesels). Factorial design evidenced a positive effect of reaction temperature, amount of catalyst, and solvents on ester conversion. This nano-sized sulfated titania has been prepared by a sol-gel hydrothermal process. This prepared sulfated titania showed high catalytic activity in direct esterification of fatty acids as well as benzoic acids with various alcohols and phenols under solvent-free conditions. This method is of great value because of its environmentally benign character, easy handling, high yields, convenient operation, and green. FT-IR studies are shown that the catalyst can be reused for acylation without loss of catalytic activity.

1. Introduction

Esterification is a great interest reaction because of its wide application to several branches of industry [1]. Esters are obtained and used in the production of plastic derivatives, in the solvent industry, perfumes, food preservatives, cosmetics, agro-chemistry and as biodiesel. The latter are typically produced by either the esterification of fatty acids or the transesterification of vegetable oil. Biodiesel is a promising non-toxic and biodegradable, renewable alternative fuel compared to petroleum diesel in the light of limited nature of fossil fuel and the environmental concerns. Due to the high price of petroleum, biodiesel is currently becoming a fast-growing market product [2–6].

Alkaline hydroxides under homogeneous condition show higher performance for obtaining biodiesel. Free fatty acids poison homogeneous catalysts such as NaOH and KOH, forming soaps, corrosive to equipment and also creating difficulties to separate the products of the reaction [7]. Another route to produce fatty esters is catalyzed by homogeneous acids such as H_2SO_4, *p*-toluenesulfonic acid, HCl, etc. However, these acid catalysts are toxic, corrosive, and are very difficult to be removed from the reaction medium [8]. For homogeneous catalysts, the problem is the high consumption of energy and costly separation of the homogeneous catalyst from the homogeneous reaction mixture, which generates more waste water [9,10]. Nowadays, the replacement of mineral acids by solid acid catalysts, in order to avoid important corrosion effects, catalyst separation and pollution problems, has been an important subject for many laboratory industrial processes worldwide [11]. Some recyclable solid acids, such as Nafion [12,13], have been reported as very active catalysts, but they are expensive and their activity is less than that of liquid acids. Some solid oxides and their sulfated forms such as Al_2O_3, SiO_2 showed some certain activity. Rotenberg et al. [14] showed various solid acid such as zeolites, ion-exchange resin and mixed metal oxides as catalyst in the etherification at high temperature 130–140 °C, finding that sulfated zirconia is a promising candidate [14]. Recently, Ropero et al. [15] and de Almeida et al. [16] reported sulfated TiO_2 as a solid acid catalyst for esterification of fatty acids with EtOH and transesterification of vegetable oils. The

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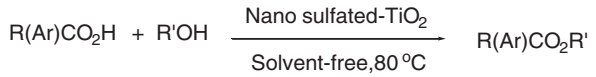
activity of this solid sulfated catalyst is more than half that of a liquid sulfuric acid catalyst. However, the esterification reaction needed to be carried out under reflux at 80 °C, a fatty acid:ethanol molar ratio 1:10 were used, and the weigh of the used catalyst was 2%. Therefore, a new family of catalyst, in order to show high activity, and recyclable is required. Nano sulfated-TiO_2 used in the present study is found to have large surface area (218 m^2/g), compared to the bulky TiO_2 and previous prepared sulfated titania reported in the literature. Also, significantly higher catalytic activity for nano sulfated-TiO_2 could be attributed to its stronger surface acidity (pK_a is evaluated to 1.911, which is in good agreement with acidic strength of sulfuric acid $pK_a2 = 2.00$) and nanometres sized and large surface area compared to the previously studied catalysts.

In general, sulfated-TiO_2 has low toxicity and shows no evidence of carcinogenicity. Therefore, sulfated-TiO_2 has attracted great interest as potential green catalyst because green catalysts require not only high catalytic activity and atom efficiently, but also low toxicity, low cost and ease of handling. With this in mind, in the present study, we report the synthesis of new nano-sized sulfated titania by the sol-gel method and its catalytic activity for esterification of fatty acids with various alcohols. The studies were performed in a very simple media, under solvent-free condition. In addition, we have conducted XRD, FT-IR, SEM, TEM, and other various techniques to determine the properties of the catalyst [17].

2. Results and discussions

The first step in this concept was the selection of method for the preparation of nano sulfated titania (nano ST). We decided to explore the sol-gel method, since it is presently a widely accepted method for the preparation of such materials [18]. The advantages of the sol-gel process in general are high purity, homogeneity and low temperature. For low temperature processes, there is a reduced loss of volatile components and thus the process is more environmentally friendly. Recently, we reported the preparation and characterization of nano ST and investigated its application in the amidation of fatty acids [17]. Therefore, herein, prepared nano ST (by using sol-gel method as shown in Fig. 1) was described as a practical, inexpensive, and environmentally benign catalyst for the esterification of free fatty acids in high yields.

At first, efforts were made to optimize the reaction conditions using nano sulfated-TiO_2 as an efficient catalyst for direct esterification of various carboxylic acids. For the determination of the effective amount of nano sulfated-TiO_2, the reaction of benzoic acid (**1a**) with *n*-butanol (**2a**) was considered as the model (Scheme 1, Table 1). When



Scheme 1.

the reactions were carried out with lower amount of the catalyst (0.005 mol %), either trace amounts of product were formed or incomplete conversion of the starting materials to the product was observed after 8 h at 80 °C. Excellent (90%) conversion to *n*-butyl-benzoate (**3a**) after 4.5 h took place with (0.011 mol %) of nano sulfated-TiO_2, at 80 °C. By increasing the amount of catalyst to 0.022 mol% the yield not only increased but also decreased. Thus, the effective/convenient catalyst loading was found to be 0.011 mol% (Table 1, entry 3). A brief screening of solvents showed that water, CH_2Cl_2, and EtOH, were less effective than toluene, MeCN, and THF solvents system (entries 5–10). So because of toxicity and volatile nature of organic solvents, the design of solvent-less catalytic reaction has received tremendous attention in present study in the area of the green synthesis.

Using the optimized reaction conditions, from Table 1 and in order to extended the scope of the reaction as a general and practical procedure for esterification, we carried out the reaction of a series of aryl, heteroaryl, aliphatic, and cycloalkane carboxylic acid with equimolar amount of primary/secondary short and long chain aliphatic, allylic, propargylic, and cycloalkyl alcohols under solvent-free conditions at 80 °C in the presence of nano sulfated-TiO_2 (0.011 mol%) (Scheme 1). The reactions were completed after 2–10 h affording good to excellent yields of the corresponding esters (Table 2). No competitive side reactions of acid sensitive substrate were observed.

As shown in Table 2, various aromatic and aliphatic carboxylic acids as well as heterocyclic with different alcohols converted to the corresponding esters in good to high yields. In most of cases, the products obtained after the usual workup was pure (spectral data) and did not require additional efforts of purification. Wherever required, the purification was performed by column chromatography. In the case of esterification of benzoic acids and its derivatives (as the carbonyl carbon of aromatic carboxylic acid is less electrophilic compared to fatty acids, and aliphatic ones) with various alcohols, the esters were obtained in good to excellent yields (entries 1–12). The efforts were made for the evaluation of mildness and efficiency of the nano sulfated-TiO_2 for the esterification of the electron-donating and electron-withdrawing substituted benzoic acid with *n*-octanol under the same reaction conditions (entries 8–10). The desired esters **3h–j** were obtained in 70, 60, and 50% yields, respectively.

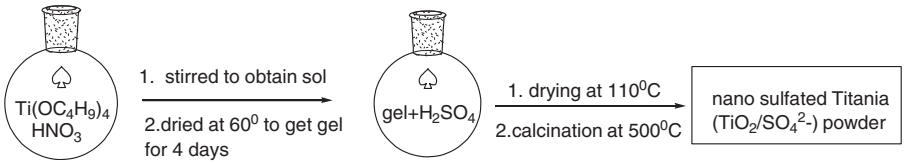
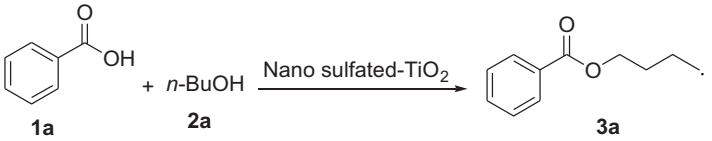


Fig. 1. Preparation process of nano sulfated titania powder.

Table 1
Optimization of reaction conditions for the synthesis of *n*-butyl benzoate (3a) using nano sulfated-TiO_2 as catalyst[a].



1a **2a** **3a**

Entry	Catalyst mol% (g)	Solvent	Time (h)	Yield (%)[b]
1	0.005 (0.1)	–	8	Trace
2	0.007 (0.1)	–	8	80
3	0.011 (0.2)	–	4.5	90
4	0.03 (0.4)	–	8	60
5	0.011 (0.2)	H_2O	4.5	Trace
6	0.011(0.2)	CH_2Cl_2	4.5	40
7	0.011(0.2)	EtOH	4.5	45
8	0.011(0.2)	$PhCH_3$	4.5	90
9	0.011(0.2)	MeCN	4.5	90
10	0.011(0.2)	THF	3.5	90

[a] Reaction conditions: benzoic acid (1 mmol), *n*-butanol (1 mmol), in an oil bath at 80 °C.
[b] Isolated yield.

Table 2
Direct esterification of various aromatic carboxylic acids with different alcohols catalyzed by nano sulfated-TiO_2[a].

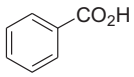
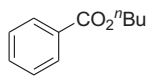
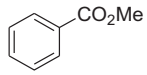
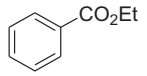
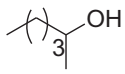
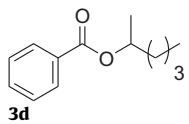
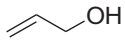
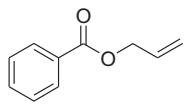
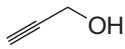
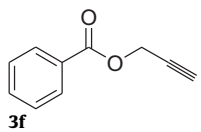
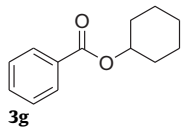
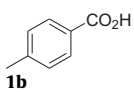
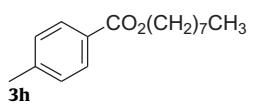
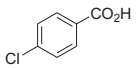
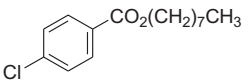
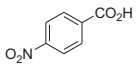
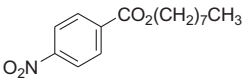
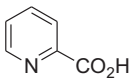
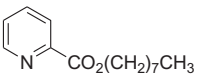
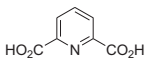
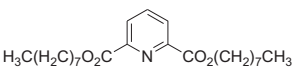
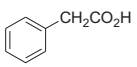
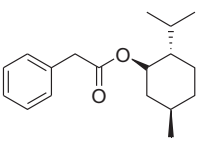
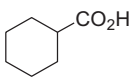
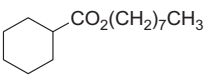
Entry	Acid	Alcohol	Ester	Time (h)	Yield (%)[b]
1	 **1a**	*n*-BuOH **2a**	 **3a**	4.5	90
2	**1a**	MeOH **2b**	 **3b**	4	90
3	**1a**	EtOH **2c**	 **3c**	4	90
4	**1a**	 **2d**	 **3d**	5.5	70
5	**1a**	 **2e**	 **3e**	9	60
6	**1a**	 **2f**	 **3f**	6	50
7	**1a**	Cyclohexanol **2g**	 **3g**	7	70
8	 **1b**	*n*-octanol **2h**	 **3h**	5	70

Table 2 (*Continued*)

Entry	Acid	Alcohol	Ester	Time (h)	Yield (%)[b]
9	 **1c**	**2h**	 **3i**	5	60
10	 **1d**	**2h**	 **3j**	5	50
11	 **1e**	**2h**	 **3k**	10	80
12	 **1f**	**2h**	 **3l**	10	60[c]
13	 **1g**	(-)menthol **2i**	 **3m**	8	70[d]
14	 **1h**	**2h**	 **3n**	2	98

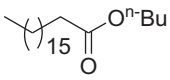
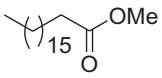
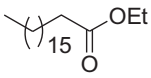
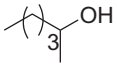
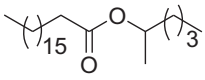
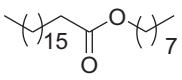
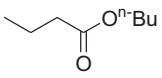
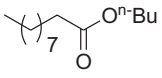
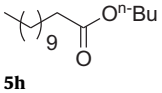
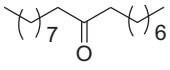
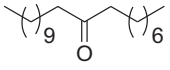
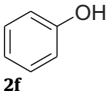
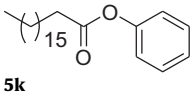
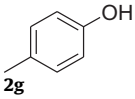
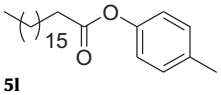
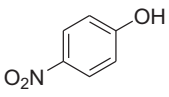
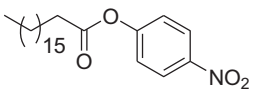
[a] Reaction condition: the carboxylic acid (1 mmol), alcohol (1 mmol), and catalyst (0.011 mol %) in an oil bath at 80 °C, under solvent-free conditions.
[b] Isolated yield.
[c] The molar ratio of acid: alcohol is 1:2.
[d] The desired ester obtained in optically pure form (based on ^{1}HNMR spectroscopy).

Further, the esterification was performed with an acid sensitive alcohols such as allylic and propargyl alcohol **2e**, **2f** affording the corresponding ester **3e, 3f** in moderate yields (entry 5, 6). Moreover, the mildness/efficiency of the nano sulfated-TiO_2 catalyzed reaction was demonstrated with hetero aromatic carboxylic and di-carboxylic acid (entries 11, 12) that resulted in the formation of the corresponding ester and di-ester in good to excellent yields, respectively. The stereo chemical influence of the reaction was then probed utilizing L-menthol as the chiral alcohol. Menthol reacts with phenyl acetic acid in solvent free conditions in presence of nano sulfated-TiO_2 to give the corresponding chiral menthol ester in good yield (entry 13). According to the ^{1}H NMR data reported [19], the stereochemistry of the reaction under our conditions is found to be with prefect retention of configuration.

Fatty acids or derivatives are used in a wide variety of applications. About one hundred thousand tonnes of the natural fatty acids are used in the preparation of various fatty acid esters. The simple esters such as methyl, ethyl, and *n*-butyl esters are used as moisturizers in cosmetics, biodiesel, etc. Esters of fatty acids with more complex alcohols such as diols, ethylene glycol, di-ethylene glycol and polyethylene glycol are used in foods, paper rolling oils, synthetic lubricants, etc. So, using a proper catalyst and simple reaction media is needed for the synthesis of fatty acid esters. Under similar conditions, we investigated the reaction of fatty acids **4** with alcohols to synthesize the corresponding esters **5**. The results were shown in Table 3.

Table 3 shows the typical result of the esterification of fatty acids such as caprylic, capric, lauric, and stearic acids with aliphatic alcohols using nano-sulfated-TiO_2 (0.011 mol %) as a catalyst. The esterification occurred efficiently for all fatty acids, resulting in the formation of corresponding fatty acid esters in high yield (98%). Nano-sulfated-TiO_2 gave ester in high yields irrespective of chain length of both fatty acid and alcohols. These tendencies are different from recent reports that catalytic activity of various catalyst increased with decrease of chain-length of substrates [20,21]. Recently, fatty acid methyl (or ethyl) esters, FAME (or FAEE) (biodiesel) have assumed great importance [22–24], so, we planned to investigate the application of nano sulfated-TiO_2 catalyst system for synthesis of FAME used as biodiesel. The nano sulfated-TiO_2 catalyzed direct esterification of stearic acid (**4a**) with MeOH and EtOH afforded FAME and FAEE, respectively, in 98% yields after 1.2 h (entries 2, 3). To compare the alcohol employed in the reaction, five different alcohols have been used: 1-butanol, ethanol, methanol, octanol, and 2-hexanol. The catalytic activity of nano sulfated-TiO_2 was not significantly influence by the chain length of alcohols (entries 1–5). The increase in the yield of **5d** than **5e** effect might be due to a steric effect on the secondary alcohol.

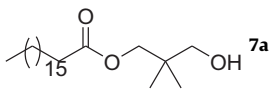
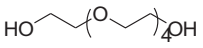
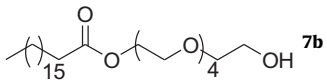
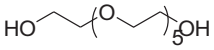
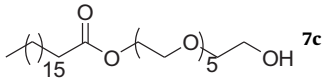
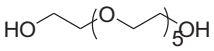
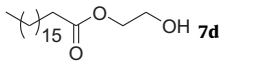
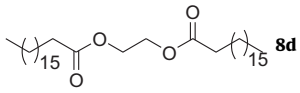
Table 3
Direct esterification of various fatty acids with alcohols and phenols catalyzed by nano sulfated-TiO_2[a].

Entry	Fatty acid	Alcohol	Ester	Time (h)	Yield (%)[b]
1	Stearic acid **4a**	*n*-BuOH **2a**	 **5a**	1.5	98
2	**4a**	MeOH **2b**	 **5b**	1.5	98
3	**4a**	EtOH **2c**	 **5c**	1.5	98
4	**4a**	 **2d**	 **5d**	1:20	90
5	**4a**	*n*-OctylOH **2e**	 **5e**	1.5	98
6	Caprylic acid **4b**	**2a**	 **5f**	1.5	98
7	Capric acid **4c**	**2a**	 **5g**	1.5	98
8	Lauric acid **4d**	**2a**	 **5h**	1.5	98
9	**4c**	**2**e	 **5i**	1.5	98
10	**4d**	**2e**	 **5j**	1.5	98
11	**4a**	 **2f**	 **5k**	9	70
12	**4a**	 **2g**	 **5l**	9	60
13	**4a**	 **2h**	 **5m**	9	80

[a] Reaction condition: the carboxylic acid (1 mmol), alcohol or phenol (1 mmol), catalyst (0.011 mol %) in an oil bath at 80 °C, under solvent free conditions.
[b] Isolated yields.

Another promising feature of this new nano sulfate TiO_2 catalyst is the efficient preparation of fatty acid ester of phenols. To the best of our knowledge, there are very few old reports concerning the context of coupling fatty acids with phenols [25]. So, to disseminate the usage of nano sulfate TiO_2, the esterification reaction between stearic acid and substituted phenols was carried out under solvent free conditions, at 80 °C (Table 3, entries 11–13).

Table 4
Direct esterification of various diols and polyol with stearic acid catalyzed by nano sulfated-TiO_2.[a]

Entry	Diol	Ester	Time (h)	Yield (%)[b]
1	 **6a**	 **7a**	4	90
2	 **6b**	 **7b**	2.5	98
3	 **6c**	 **7c**	2	98
4	 **6d**	 **7d**  **8d**	1.5	1.5/98 (50:50)[c]

[a] Reaction condition: The carboxylic acid (1 mmol), diol or polyol (1 mmol), catalyst (0.011 mol %) in an oil bath at 80 °C, under solvent free conditions.
[b] Isolated yields.
[c] The ratio was determined by ^{1}HNMR.

In order to investigate and generalized the reaction condition, we then choosing a range of diols and polyols in the reaction with stearic acid (Table 4). As shown in Table 4, various diols and polyols were esterifies with stearic acid to produce the corresponding esters. In the case of neopentyl glycol, hexa and penta ethylene glycols the selectivity was observed and only the mono ester was produced (**7a–c**). However, when 1, 2-ethandiol was esterified by stearic acid both mono and di-stearates were obtained in 50:50% yields, respectively (entries **7d, 8d**).

The catalyst in the esterification reaction of benzoic acid with *n*-butanol was easily recovered by dilution of the reaction mixture with EtOAc and centrifugation according to XRD and FTIR spectroscopy. The catalyst was reused, producing 90, 87, 85, 85, and 73% *n*-butyl benzoate after the first, second, third, forth, and fifth reuse, respectively (Table 5).

FT-IR and XRD patterns of nano sulfated titania before and after using in the reaction are shown in Figs. 2 and 3a shows the XRD patterns of fresh prepared nano sulfated titania which was retained after the first reuse (Fig. 2b).

FTIR spectroscopy of fresh nano sulfated titania is shown in Fig. 3a. Four bands in the region between 1230 and 980 cm^{-1} attributed to vibrational modes of bidentate sulfate ions can be seen. Two bands at 1221 and 1138 cm^{-1} appear due to asymmetric and symmetric stretching of S=O vibrations, respectively. The band around 1047 cm^{-1} is attributed to the asymmetric S–O bond. The band at 993 cm^{-1} is related to the symmetric stretching of the S–O bond. All of these bands are related to the sulfate bounds to the TiO_2 in the chelate form. The bands at 1626 and 3347 cm^{-1} are, respectively, associated with the bending and stretching vibrations of the OH group of water molecules on the surface of the solid [16].

Table 5
Reusability of nano sulfated-TiO_2 in the esterification of benzoic acid with *n*-butanol.

Entry	Catalyst use	Time (h)	Yield (%)[a]
1	Fresh	4.5	90
2	1st recycle	5	90
3	2nd recycle	5	87
4	3rd recycle	6	85
5	4th recycle	6	85
6	5th recycle	10	73

[a] Isolated yield

The FTIR spectrum of the catalyst recovered after first, third, and fifth reaction showed two clear bands for the bending and stretching vibrations of the OH group of water molecules which was shown that the water molecule can be adsorbed during the work-up procedure. However, after fifth recovered catalyst the bands in the range of 990–1221 cm^{-1} which indicate the sulfonyl group has begun to disappear. Therefore, due to the leaching of the sulfate in the catalyst, the yield was decreased after fifth recycling.

In conclusion, the production of biodiesel fuel from esterification of fatty acid with MeOH or EtOH using nano sulfated-TiO_2 as a catalyst was investigated in the present study. The nano sulfated-TiO_2 was obtained by sol-gel method and characterized in terms of its acidity, and structural aspects. In addition, this catalyst is very active in the esterification of fatty acids and aromatic/aliphatic carboxylic acids with various alcohols. The advantages are as follows: (a) the use of a cheap and easy prepared catalyst, (b) solvent free condition, (c) short reaction times and high yields, (d) easy reaction procedure, and workup, (e) use very low catalytic amount of catalyst (0.011 mol%), and (f) both component (acid and alcohol) are taken in stoichiometric amounts in order to avoid environmental waste fulfil the philosophy of green chemistry.

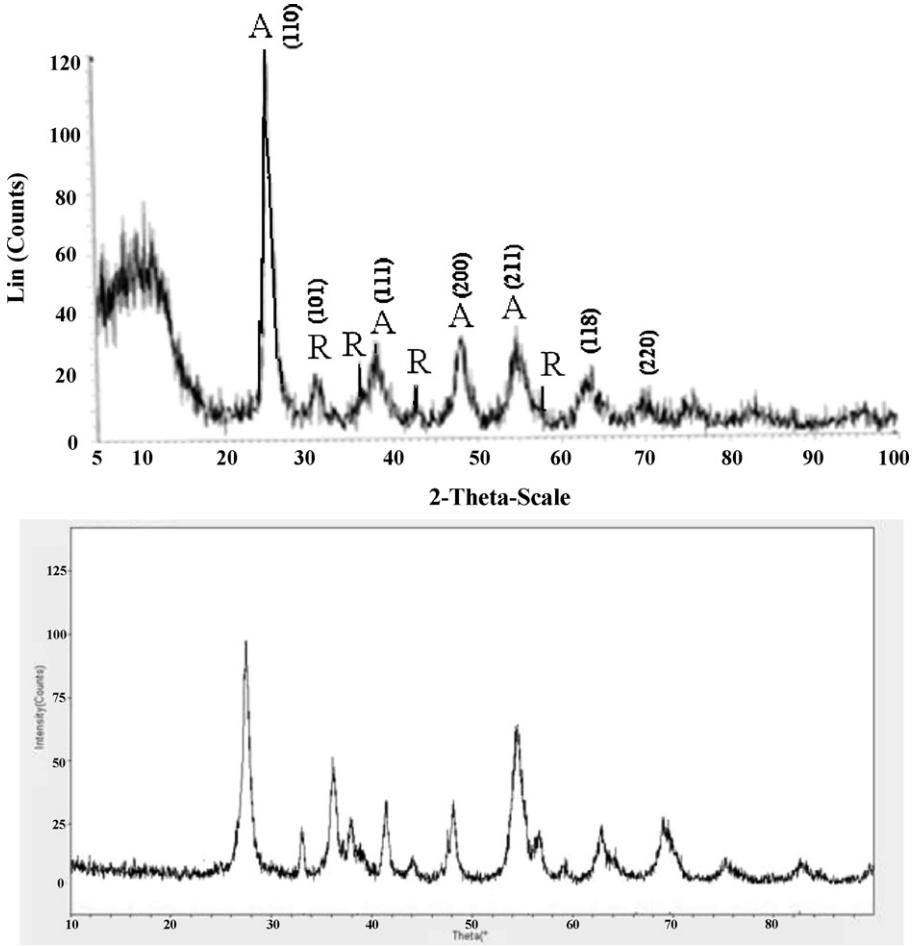


Fig. 2. XRD patterns of nano sulfated titania (a) fresh (b) after second reuse.

3. Experimental part

Tetra butyl ortho-titanate monomer ($C_{16}H_{36}O_4Ti$), carboxylic acid, alcohols and phenols were purchased from Merck, Fluka, Aldrich, or Across Companies.

Chemicals were purchased from Fluka, Merck, B. D. H., and Aldrich Chemical Companies. TLC Monitoring: silica gel Polygrams SIL G/UV 254 plates. ^{1}H NMR and ^{13}C NMR spectra were measured on Bruker Advance DPX FT 250 and 62.9 MHz spectrometry with TMS as an internal standard. Mass spectra were obtained on a Shimadzu GCMS0QP 1000EX at 20 and/or 70 eV.

3.1. Catalyst preparation

Sulfated titania nano powders were prepared by sol-gel process. Titanium isobutoxide (98% Aldrich) was used as the source of titania. An amount, 14.3 ml, of Ti $(OC_4H_9)_4$ was hydrolyzed in 150 ml water containing 1.25 ml nitric acid (65% Merck). Precipitates formed were stirred continuously at room temperature fore 2 h to form a highly dispersed sol, then the sol was concentrated and dried at 60 °C for 4 days. Sulfation was done using 0.5 M sulfuric acid solution (2 g ml^{-1} of the hydroxide). The samples, after 2 h drying at 110 °C, were calcined for 5 h at 500 °C [17].

3.2. Catalyst characterization

Power X-ray diffraction (XRD) was performed on a Bruker D8-advance X-ray diffractometr with Cu Ka (λ = 1.54178 Å) radiation. The FT-IR spectra were recorded on an impact 400D Nickolet FT-IR spectrophotometer. The morphology of the products were determined by using a Leica Cambbridge, model s360, version V03.03 Scanning electron microscopy (SEM), performed at accelerating voltage of 25 Kv. The size of nano flakes were confirmed using a Philips CM10 TEM instrument [17]. In this study, conductometric analysis was used to evaluate the acidity of the synthesized catalyst. In accordance with the conductometric results, the pK_a is evaluated to 1.911, which is in good agreement with acidic strength of sulfuric acid (pK_a2 = 2.00). According to the Hammett-type acidity functions (H_0), the amount of acidity was estimated to ~1.916.

3.3. Esterification of carboxylic acids with alcohol

Esterification reaction was performed in experimental tube at atmospheric pressure by using a condenser and equipped with a Teflon-coated magnet stirring bar. The mixture of carboxylic acid (1 mmol), alcohol or phenol

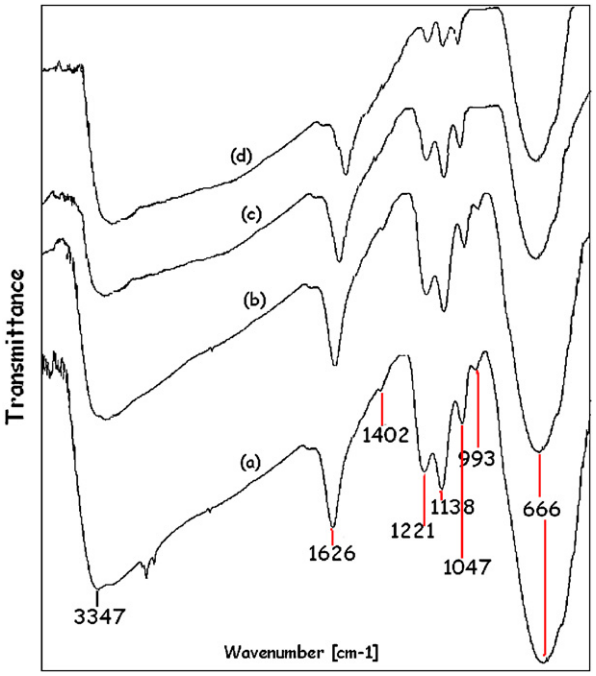


Fig. 3. FT-IR spectra of the (a) nano sulfated titania (b) recovered after first (c) third and (d) fifth reuse.

(1 mmol) and nano sulfated-TiO_2 (0.2 g, 0.011 mol %) were stirred magnetically at 80 °C until complete, monitored by TLC or GC. The reaction mixture was diluted with EtOAC (10 mL) and centrifuged to remove the catalyst. The filtrate was washed with satd. aq. $NaHCO_3$ (3 × 5 mL) and water (3 × 5 mL) dried over $CaCl_2$ and concentrated under vacuum. The identity and purity of the product was confirmed by NMR, MASS, and IR spectroscopic.

n-Butyl benzoate (3a): Yellow liquid; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.95 (3H, t, J = 7.26 Hz, $-CH_2CH_3$), 1.56 (2H, m, CH_3CH_2-), 1.69 (2H, m, $-CO_2-CH_2-CH_2-$), 4.23 (2H, t, J = 6.58 Hz, $-CO_2CH_2-$), 7.45–7.54 (3H, m, Ar–H), 8.04 (2H, d, J = 8.34 Hz, Ar–H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.73, 19.25, 30.76, 64.76, 128.27, 129.49, 130.51, 166.61; IR cm^{-1}: (Liq.) 1720 (C═O), 2951 –(CH_2)–; MS: m/z (%) = 178 (9.9) [M^+].

Ethyl benzoate (3c): Yellow liquid; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.24 (3H, t, J = 7.84 Hz, $PhCO_2CH_2CH_3$), 4.23 (2H, m, $-CO_2CH_2CH_3$), 7.23–7.37 (3H, m, Ar–H), 7.89 (2H, d, J = 8.56 Hz, Ar–H); ^{13}C NMR (62.9 MHz $CDCl_3$): δ = 14.20, 60.76, 128.49, 129.7, 132.68, 133.14, 166.38; IR cm^{-1}: (Liq.) 1730 (C═O), 2960 –(CH_2)–; MS: m/z (%) = 150 (14.7) [M^+].

Hexan-2-ylbenzoate (3d): Yellow liquid; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.91 (3H, t, J = 6.91 Hz, $-CH_2CH_3$), 1.33–1.44 (7H, m, CH_3–CH–$CH_2(CH_2)_2CH_3$), 1.76 (2H, m,„–CO_2CHCH_2-), 4.23 (1H, m, $-CO_2CHCH_2-$), 7.40–7.54 (3H, m, Ar–H), 8.05 (2H, d, J = 8.24 Hz, Ar–H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.98, 22.54, 25.70, 28.68, 31.46, 65.08, 128.27, 128.56, 129.18, 129.50, 130.07, 132.73, 136.62; IR cm^{-1}: (Liq.) 1730 (C═O), 2967 –(CH_2)–; MS: m/z (%) = 207 (9.9) [M^+ + 1]

Allyl benzoate (3e): Brown liquid; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 4.92 (2H, m, O–CH_2–), 5.24 (2H, m, –CH_2–), 5.60 (1H, m, –CH–), 7.33–7.37 (2H, m, Ar–H), 7.43–47 (1H, m Ar–H), 7.95–7.98 (2H, m, Ar–H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 67.10, 116.40, 129.90, 133.6, 166.00 some peaks were overlapped, IR cm^{-1}: (Liq.) 1715 (C═O), 2932 (CH), 3100 (–C═CH); MS: m/z (%) = 163 (31.2) [M^+ + 1].

Pro-2-ynyl-benzoate (3f): Brown liquid; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.44 (1H, $PhCO_2CH_2CCH$) 4.91 (2H, s, $PhCO_2CH_2CCH$), 7.40–7.46 (3H, m, Ar–H), 8.05 (2H, d, J = 8.56 Hz, Ar–H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 52.42, 68.71, 75.05, 128.42, 129.37, 129.78, 129.87, 133.32, 133.44, 165.76; IR cm^{-1}: (Liq.).) 1712 (C═O), 2932 (CH), 3058 (–CCH); Ms m/z 160 (M^+). MS: m/z (%) = 161 (25) [M^+ + 1]

Cyclohexyl benzoate (3 g): Yellow liquid; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.31–1.45 (6H, m, cyclohexyl), 1.55–1.85 (4H, m, cyclohexyl), 4.96 (1H, m, cyclohexyl), 7.35–7.38 (3H, m, Ar–H), 7.97 (2H, d, J = 8.50 Hz, Ar–H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 22.63, 28.72, 34.39, 70.92, 128.54, 129.50, 130.53, 137.71, 166.53, some peaks were overlapped, IR cm^{-1}: (Liq.) 1716 (C═O), 2902 –(CH_2)–; MS: m/z (%) = 203 (13.6) [M^+−1]

n-Octyl-4-methyl benzoate (3 h): Yellow liquid. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.9 (3H, t, J = 6.25 Hz, $CH_3(CH_2)_7-$), 1.28 (10H, m, $CH_3(CH_2)_5-$), 1.73–1.78 (2H, m, $-CO_2CH_2CH_2-$), 2.4 (3H, s, CH_3–Ar), 4.24 (2H, t, J = 6.62 Hz, $-CO_2CH_2-$), 7.23 (2H, d, J = 8.18, Ar–H), 7.93 (2H, d, J = 7.97, Ar–H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.07, 21.59, 22.64, 26.05, 28.74, 29.71, 31.79, 64.91, 127.79, 128.99, 129.54, 143.34, 166.71, some peaks were overlapped; IR cm^{-1}: (Liq.) 1730 (C═O), 2962 –(CH_2)–; MS: m/z (%) = 248 (6.1) [M^+].

n-Octyl-4-choloro benzoate (3i): Yellow liquid. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.84 (3H, t, J = 6.38 Hz, $CH_3(CH_2)_7-$), 1.21–1.37 (10H, m, $CH_3(CH_2)_5-$), 1.66–1.77 (2H, m, $-CO_2CH_2CH_2-$), 4.24 (2H, t, J = 7.00 Hz, $-CO_2CH_2-$), 7.18 (2H, d, J = 8.78 Hz, Ar–H), 8.11 (2H, d, J = 8.62 Hz, Ar–H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.71, 22.44, 26.00, 29.01, 29.33, 31.58, 65.60, 127.68, 129.00, 130.58, 138.88, 165.08 some peaks were overlapped; IR cm^{-1}: (Liq.) 1730 (C═O), 2958 –(CH_2)–; MS: m/z (%) = 168.5 (5.8) [M^+].

n-Octyl-4-nitro benzoate (3j): Yellow liquid. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.81 (3H, t, J = 6.92 Hz, $CH_3(CH_2)_7-$), 1.21–1.38(10H, m, $CH_3(CH_2)_5-$), 1.63–1.74 (2H, m, $-CO_2CH_2CH_2-$), 4.23 (2H, t, J = 6.67 Hz, $-CO_2CH_2-$) 7.35 (2H, d, J = 8.75 Hz, Ar–H), 7.90 (2H, d, J = 8.62 Hz, Ar–H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.02, 22.60, 25.95, 29.14, 29.25, 29.44, 66.07, 123.46, 130.61, 135.85, 150.43, 164.69, some peaks were overlapped; IR cm^{-1}: (Liq.) 1737 (C═O), 2952 –(CH_2)–; MS: m/z (%) = 279 (0.8) [M^+].

n-Octyl piconilate (3k): Yellow liquid. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.85 (3H, t, J = 6.51 Hz, $CH_3(CH_2)_7-$), 1.37 (10H, m, $CH_3(CH_2)_5-$), 1.74–1.86 (2H, m, $-CO_2CH_2CH_2-$), 4.26 (2H, t, J = 6.66 Hz, $-CO_2CH_2-$), 7.45 (1H, m, Ar–H), 7.82 (1H, m, Ar–H), 8.09 (1H, d, J = 8.77 Hz, Ar–H), 8.73 (1H, m, Ar–H); ^{13}C NMR (62.9 MHz $CDCl_3$): δ = 14.05, 22.59, 25.86, 28.64, 29.12, 31.74, 66.11, 125.07, 126.77, 137.00, 148.22, 149.81, 165.55 some peaks were overlapped; IR cm^{-1}: (Liq.) 1738 (C═O), 2922 –(CH_2)–; MS: m/z (%) = 235 (0.4) [M^+].

n-Octyl-6-(octanoyloxy) piconilate (3l): Viscose liquid; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.81 (6H, t, J = 6.72 Hz, $2CH_3(CH_2)_7-$), 1.19–1.75 (20H, m, $2CH_3(CH_2)_5-$), 1.33–1.78

(4H, m, 2–$CO_2CH_2CH_2$–), 4.30 (4H, t, J = 6.79 Hz, 2–CO_2CH_2–), 7.89–7.95 (1H, m, Ar–H), 8.16–8.19 (2H, d, J = 7.71 Hz, Ar–H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.01, 22.57, 25.84, 28.50, 29.11, 31.72, 66.28, 127.63, 138.07, 148.66, 164.60 some peaks were overlapped; IR cm^{-1}: (Liq.) 1751 (C=O), 2962 –(CH_2)–; MS: m/z (%) = 391 (1.9) [M$^+$].

(1s,2s)-2-Isopropyl-5-methylcyclohexyl-2-phenylacetate(3 m): Yellow liquid; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.68 (3H, s, –CH_3), 0.7 (3H, s,–CH_3), 0.83 (3H, s, –CH_3), 1.7 (8H, m, cyclohexyl), 1.95 (1H, m, cyclohexyl), 3.60 (2H, s, –CH_2–CO_2–), 4.63–4.73 (1H, dt, J_1 = 4.41, J_2 = 10.85 Hz, –CO_2CH–), 7.21–7.65 (5H, m, Ar–H–); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 16.212, 20.68, 21.93, 23.86, 26.10, 31.36, 34.23, 40.76, 41.83, 47.02, 74.67, 126.91, 128.44, 129.15, 133.4, 171.16, some peaks were overlapped; IR cm^{-1}: (Liq.) 1739 (C=O), 2966 (CH); MS: m/z (%) = 274 (2.8) [M$^+$−1].

n-Octyl cyclohexanoate (3n): Yellow liquid; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.56 (3H, t, J = 6.27 Hz, $CH_3(CH_2)_7$–), 0.9–0.98 (22H, m, cyclohexyl, $CH(CH_2)_5$–), 1.94–1.96 (1H, m, cyclohexyl), 3.75 (2H, t, J = 5.36 Hz, –CH_2CO_2–); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.86, 22.49, 24.87, 25.44, 26.10, 28.56, 28.90, 29.06, 29.67, 31.66, 32.71, 34.15, 43.06, 63.06, 175.71, some peaks were overlapped. IR cm^{-1}: (Liq.) 1737 (C=O), 2952 –(CH_2)–; MS: m/z (%) = 240 (14.2) [M$^+$].

n-Butyl stearate (5a): Viscose liquid; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.89 (6H, t, J = 7.31 Hz, 2- CH_2CH_3), 1.22 (30H, m, $CH_3(CH_2)_{14}CH_2$–, –$CO_2(CH_2)_2CH_2CH_3$), 1.51–1.62 (4H, m, –$CH_2CH_2CO_2CH_2CH_2$–), 2.24 (2H, t, J = 7.49 Hz, –CH_2CO_2Bu), 4.05 (2H, t, J = 6.62 Hz, –$CO_2CH_2CH_2$–); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.59, 14.00, 19.08, 22.62, 24.94, 27.90, 29.10, 29.22, 29.31, 29.41, 29.55, 29.64, 30.66, 31.87, 34.27, 63.93, 173.76, some peaks were overlapped; IR cm^{-1}: (Liq.) 1745 (C=O), 2939 –(CH_2)–; MS: m/z (%) = 340 (2.3) [M$^+$].

Methyl stearate (5b): Viscose liquid; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.63 (3H, t, J = 7.07 Hz, – CH_2CH_3), 1.06 (28H, m, $CH_3(CH_2)_{14}CH_2$–), 1.32–1.38 (2H, m, –$CH_2CH_2CO_2$–), 2.06 (2H, t, J = 7.60 Hz, –CH_2CO_2Me), 3.37 (3H, s, –CO_2CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.01, 14.14, 22.63, 24.92, 29.10, 29.23, 29.32, 29.42, 29.56, 29.65, 32.17, 32.88, 33.65, 34.27, 59.98, 173.68, some peaks were overlapped; IR cm^{-1}: (Liq.) 1739 (C=O), 2923 –(CH_2)–; MS: m/z (%) = 298 (2.6) [M$^+$].

Ethyl stearate (5c): Viscose liquid; 1H NMR (250 MHz, CDCl3): δ = 0.64 (3H, t, J = 7.09 Hz, – CH_2CH_3), 1.10 (28H, m, $CH_3(CH_2)_{14}CH_2$–),1.34–1.39 (5H, m,–$CH_2CH_2CO_2CH_2$–CH_3), 2.08 (2H, t, J = 7.51 Hz, – CH_2CO_2Et), 4.12 (2H, t, J = 6.62 Hz,–$CO_2CH_2CH_3$); 13 C NMR (62.9, MHz $CDCl_3$): δ = 14.01, 14.14, 22.63, 24.92, 29.10, 29.23, 29.32, 29.42, 29.56, 29.65, 32.17, 32.88, 33.65, 34.27, 59.98, 173.68, some peaks were overlapped; IR cm^{-1} (Liq.) 1739 (C=O), 2923 –(CH_2)–; MS: m/z (%) = 312 (2.6) [M +].

Hexan-2-yl stearate (5d): Viscose liquid; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.68 (6H, t, J = 6.80 Hz, 2– CH_2CH_3), 1.05 (37, m, $CH_3(CH_2)14CH_2$–, CH_3–CH–$(CH_2)3$), 1.66–1.82 (2H, m, –$CH_2CH_2CO_2$–), 2.14 (2H, t, J = 7.32 Hz, –CH_2CO_2–), 3.85 (1H, m, –CO_2CHCH_2–); 13 C NMR (62.9 MHz, CDCl3): δ = 13.95, 14.08, 22.51, 22.67, 25.00, 25.58, 28.59, 29.04, 29.14, 29.25, 29.34, 29.42, 29.58, 29.67, 31.41, 31.90, 34.38, 64.38, 174.03, some peaks were overlapped; IR cm^{-1}: (Liq.) 1743 (C=O), 2941 –(CH_2)–; MS: m/z (%) = 368 (4.9) [M +].

n-Octyl stearate (5e): Viscose liquid; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.88 (6H, t, J = 7.06 Hz, 2– CH_2CH_3), 1.25 (36H, m, $CH_3(CH_2)_{14}CH_2$–, $CH_3(CH_2)_5CH_2$–), 1.56–1.64 (4H, m, –$CH_2CH_2CO_2CH_2CH_2$–), 2.28 (2H, t, J = 7.33 Hz, –CH_2CO_2–), 4.05(2H, t, J = 4.46 Hz, –$CO_2CH_2CH_2$–); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.05, 22.61, 22.67, 23.44, 25.01, 25.92, 28.63, 29.14, 29.17, 29.25, 29.34, 31.76, 31.90, 34.39, 39.35, 64.37, 173.32, some peaks were overlapped; IR cm^{-1}: (Liq.) 1743 (C=O), 2939 –(CH_2)–; MS: m/z (%) = 396 (2.3) [M$^+$].

n-Butyl octanoate (5f): Viscose liquid; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.88 (6H, t, J = 6.46 Hz, 2- CH_2CH_3), 1.26 (10H, m, CH_3–$(CH_2)_4$–CH_2–, –$CO_2(CH_2)_2CH_2CH_3$), 1.53–1.63 (4H, m, –$CH_2CH_2CO_2CH_2CH_2$–), 2.24 (2H, t, J = 7.46 Hz, –CH_2CO_2Bu), 4.05 (2H, t, J = 6.56 Hz, –$CO_2CH_2CH_2$–); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.66, 14.00, 19.11, 22.55, 24.98, 29.07, 29.66, 30.67, 31.63, 34.36, 64.04, 174.00; IR cm^{-1}: (Liq.) 1739 (C=O), 2960 –(CH_2)–; MS: m/z (%) = 201 (4.6) [M$^+$ + 1].

n-Butyl decanoate (5 g): Viscose liquid; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.70 (6H, t, J = 6.36 Hz, 2– CH_2CH_3), 1.01 (14H, m, CH_3–$(CH_2)_6CH_2$–, –$CO_2(CH_2)_2CH_2CH_3$), 1.32–1.38 (4H, m, –$CH_2CH_2CO_2CH_2CH_2$–), 2.28 (2H, t, J = 7.40 Hz, –CH_2CO_2Bu), 3.81 (2H, t, J = 6.62 Hz, –$CO_2CH_2CH_2$–); ^{13}C NMR (62.9 MHz $CDCl_3$): δ = 12.81, 14.42, 19.01, 22.81, 24.83, 26.7, 27.07, 29.13, 30.55, 31.12, 31.73, 36.11, 65.95, 173.32; IR cm^{-1}: (Liq) 1747 (C=O), 2933 –(CH_2)–; MS: m/z (%) = 228 (2) [M$^+$]

n-Butyl dodecanoate (5 h): Viscose liquid; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.71 (6H, t, J = 6.07 Hz, 2– CH_2CH_3), 0.95 (18H, m, CH_3–$(CH_2)_8$–CH_2–, –$CO_2(CH_2)_2CH_2CH_3$), 1.29(4H, m, –$CH_2CH_2CO_2CH_2CH_2$–), 1.99 (2H, t, J = 7.48 Hz, –CH_2CO_2Bu), 3.74 (2H, t, J = 6.70 Hz, –$CO_2CH_2CH_2$–); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.45, 13.84, 18.99, 22.52, 24.84, 29.02, 29.47, 29.15, 29.21, 29.34, 30.61, 31.78, 34.10, 63.71, 173.42; IR cm^{-1}: (Liq.) 1745 (C=O), 2939 –(CH_2)–; MS: m/z (%) = 256 (2.4) [M$^+$].

n-Octyl decanoate (5i): Viscose liquid; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.86 (6H, t, J = 6.42 Hz, 2- CH_2CH_3), 1.10 (20H, m, CH_3–$(CH_2)_6CH_2$–, $CH_3(CH_2)_4CH_2$–), 1.54–1.62 (6H, m, –$CH_2CH_2CO_2CH_2$ $(CH_2)_2$–), 2.28 (2H, t, J = 7.37 Hz, –CH_2CO_2–), 4.05 (2H, t, J = 6.69 Hz, –$CO_2CH_2CH_2$–); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.02, 22.59, 22.62, 24.73, 24.99, 25.90, 28.62, 29.12, 29.15, 29.18, 29.24, 29.39, 31.75, 31.83, 33.70, 34.36, 64.32, 173.92; IR cm^{-1}: (Liq.) 1737 (C=O), 2931 –(CH_2)–; MS: m/z (%) = 284 (2.1) [M$^+$].

n-Octyl dodecanoate (5j): Viscose liquid; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.86 (6H, t, J = 6.07 Hz, 2- CH_2CH_3), 1.26 (26H, m, CH_3–$(CH_2)_8$–CH_2–, –CH_3–$(CH_2)_5CH_2$–), 1.58–1.61(4H, m, –$CH_2CH_2CO_2CH_2CH_2$–), 2.28 (2H, t, J = 7.49 Hz, –CH_2CO_2–), 4.05(2H, t, J = 6.70 Hz, –$CO_2CH_2CH_2$–); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.05, 22.61, 22.64, 25.01, 25.91, 28.63, 29.14, 29.16, 29.19, 29.24, 29.40, 31.76, 31.84, 34.40, 64.38, 174.03, some peaks were overlapped; IR cm^{-1}: (Liq.) 1741 (C=O), 2918 –(CH_2)–; MS: m/z (%) = 312 (14.9) [M$^+$].

Phenyl stearate (5k): White solid; mp: 49–50 °C (Lit.[25] 50–51 °C); 1H NMR (250 MHz, CDCl3): δ = 0.80 (3H, t, J = 6.40 Hz, –CH_2CH_3), 1.28 (28H, m, $CH_3(CH_2)_{14}CH_2$–), 1.61–1.67 (2H, m, –$CH_2CH_2CO_2$–), 2.46 (2H, t, J = 7.47 Hz, –CH_2CO_2–), 7.00 (2H, d, J = 7.50 Hz, Ar–H), 7.12–7.16 (1H, m, Ar–H), 7.25–7.31 (2H, m, Ar-H); ^{13}C

NMR (62.9 MHz, $CDCl_3$): δ = 14.12, 22.70, 24.96, 29.38, 29.48, 29.61, 29.67, 29.71, 31.94, 34.40, 121.57, 125.67, 129.36, 150.78, 172.28, some peaks were overlapped; IR cm^{-1}: (Liq.) 1754 (C=O), 2932 –(CH_2)–; MS: m/z (%) = 360 (0.70) [M +]

p-Tolyl stearate (5l): White solid; mp: 108 °C (Lit.[26] 110 °C); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.80 (3H, t, J = 6.84 Hz, –CH_2CH_3), 1.18 (28H, m, CH_3–(CH_2)$_{14}$–CH_2–), 1.63–1.69 (2H, m, –CH_2–CH_2CO_2–), 2.23 (3H, s, Ar–CH_3), 2.28 (2H, t, J = 7.40 Hz, –CH_2CO_2–), 6.85 (2H, d, J = 7.59 Hz, Ar–H), 7.04–7.06 (2H, d, J = 8.36 Hz, Ar–H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.12, 20.84, 22.70, 24.98, 29.12, 29.26, 29.37, 29.47, 29.60, 29.70, 31.93, 34.40, 121.23, 129.87, 135.27, 148.51, 172.53, some peaks were overlapped; IR cm^{-1}: (KBr.) 1749 (C=O), 2932 –(CH_2)–; MS: m/z (%) = 374 (0.30) [M^+].

4-Nitro-phenyl Stearate (5 m): White solid; mp: 68 °C (Lit.[27] 66.5-67.5-°C); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.63 (3H, t, J = 7.62 Hz, –CH_2CH_3), 1.01 (28H, m, CH_3 (CH_2)$_{14}$$CH_2$–), 1.37–1.39 (2H, m, –$CH_2CH_2CO_2$–), 2.12 (2H, t, J = 7.30 Hz, –CH_2CO_2–), 6.68 (2H, d, J = 8.28 Hz, Ar–H), 7.90 (2H, d, J = 7.93 Hz, Ar–H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.08, 22.67, 24.67, 27.09, 29.03, 29.20, 29.35, 29.41, 29.57, 31.91, 34.10, 34.35, 115.71, 122.46, 125.23, 126.26, 141.21, 162.03, 180.56, some peaks were overlapped; IR cm^{-1}: (KBr.) 1735 (C=O), 2922 –(CH_2)–;. MS: m/z (%) = 405 (0.40) [M^+].

2-Hydroxyethyl stearate (7d): White solid; mp: 61 °C (Lit.[28] 59.5–60.5 °C); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.87 (3H, t, J = 6.35 Hz, –CH_2CH_3), 1.18 (28H, m, CH_3 (CH_2)$_{14}$$CH_2$–) 1.55 (2H, m, –$CH_2CH_2CO_2$–), 2.23 (1H, s, –OH), 2.28 (2H, t, J = 6.40 Hz, –CH_2CO_2–), 3.62 (2H, t, J = 6.27 Hz –CH_2OH), 4.41(2H, t, J = 6.06 Hz, –CO_2CH_2-CH_2OH); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.08, 22.66, 24.88, 29.11, 29.25, 29.34, 29.55, 29.59, 29.63, 29.67, 31.90, 34.16, 63.17, 69.09, 173.73, some peaks were overlapped; IR cm^{-1}: (KBr) 1730 (C=O), 2922 –(CH_2)–, 3300 (OH); MS: m/z (%) = 327 (2.3) [M^+−1]

2-[(1-Heptadecyleth-1-enyl)oxy]ethylstearate (8d): Viscose liquid; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.87 (6H, t, J = 6.26 Hz, 2-CH_2CH_3), 1.25 (56H, m, 2 CH_3(CH_2)$_{14}$$CH_2$–), 1.58–1.61 (4H, m, 2–$CH_2CH_2CO_2$–), 2.31 (4H, t, J = 7.43 Hz, 2–CH_2CO_2–), 4.25(4H, s, –OCH_2CH_2O–); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.09, 22.67, 24.88, 29.10, 29.26, 29.35, 29.46, 29.61, 29.65, 29.68, 31.91, 34.12, 61.95, 173.56, some peaks were overlapped; IR cm^{-1}: (Liq) 1739 (C=O), 2912 –(CH_2)–; MS: m/z (%) = 594 (1.7) [M^+].

3-Hydroxy-2,2-dimethylpropyl stearate (7a): Viscose liquid; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.86 (3H, t, J = 6.96 Hz, –CH_2CH_3), 0.89 (6H, s, –$CO_2CH_2C(CH_3)_2CH_2$OH), 1.12 (28H, m, CH_3(CH_2)$_{14}$$CH_2$–), 1.56–1.62 (2H, m, –$CH_2CH_2CO_2$–), 2.30 (2H, t, J = 7.38 Hz, –CH_2CO_2–), 2.52(4H, s, OH), 3.26 (2H, s, –CH_2OH), 3.90 (2H, s, –CO_2CH_2–); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.07, 21.43, 21.70, 22.65, 25.00, 29.13, 29.21, 29.32, 29.42, 29.56, 29.65, 31.88, 34.29, 36.36, 68.12, 69.16, 174.56, some peaks were overlapped; IR cm^{-1}: (Liq) 1734 (C=O), 2922 –(CH_2)–, 3495.20 (OH); MS: m/z (%) = 370 (12.5) [M^+].

13-Hydroxy-3,6,9,12-tetraoxatridecyl stearate (7b): Viscose liquid; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.85(3H, t, J = 6.58 Hz, –CH_2CH_3), 1.21–1.29 (28H, m, CH_3(CH_2)$_{14}$$CH_2$–), 1.54–1.57 (2H, m, –$CH_2$–$CH_2CO_2$–), 2.25–2.31 (2H, t, J = 7.35 Hz, CH_3(CH_2)$_{15}$$CH_2CO_2$–), 3.59 (1H, s, –OH), 3.60–3.67 (18H, m, –$CO_2CH_2CH_2O$(CH_2CH_2O)$_4$–), 4.18 (2H, t, J = 6.48 Hz, –CO_2CH_2–); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.06, 22.63, 25.01, 25.91, 28.63, 29.18, 29.24, 29.40, 31.75, 31.83, 34.39, 63.36, 64.36, 70.20, 72.54, 173.78, some peaks were overlapped; IR cm^{-1}: (Liq.) 1747 (C=O), 2921 –(CH_2)–, 3525 (OH); MS: m/z (%) = 504 (12.3) [M^+].

17-Hydroxy-3,6,9,12,15-tetraoxatridecyl stearate (7c): Viscose liquid; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.87 (3H, t, J = 6.31 Hz, –CH_2CH_3), 1.24–1.25 (28H, m, CH_3(CH_2)$_{14}$$CH_2$–), 1.60 (2H, m, –$CH_2CH_2CO_2$–), 2.28–2.36 (2H, t, J = 6.38 Hz, CH_3(CH_2)$_{15}$$CH_2CO_2$–), 3.59 (1H, s, –OH), 3.48–3.57 (22H, m, –$CO_2CH_2CH_2O$(CH_2CH_2O)$_5$–), 4.13 (2H, t, J = 6.03 Hz, –CO_2CH_2–); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.07, 22.64, 24.86, 29.09, 29.23, 29.32, 29.43, 29.57, 29.61, 29.65, 31.88, 34.15, 60.61, 61.59, 61.98, 62.34, 63.30, 69.15, 70.20, 70.47, 70.53, 70.57, 72.54, 173.78, some peaks were overlapped; IR cm^{-1}: (Liq.) 1743 (C=O), 2939 –(CH_2)–, 3544 (OH); MS: m/z (%) = 548 (11.3) [M^+].

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