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Nano Sulfated Titania as Solid Acid Catalyst in Direct Synthesis of Fatty Acid Amides

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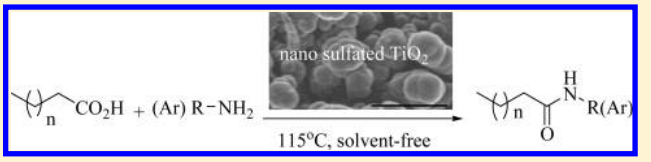
Supporting Information

ABSTRACT: Nanosized sulfated titania was prepared by a sol−gel hydrothermal process. X-ray diffraction (XRD), transmission electron, and scanning electron micrographs (TEM and SEM), FT-IR specific surface area, and BET N_2 adsorption were employed to characterize the properties of the synthesized sulfated TiO_2. The results indicate that both anatase and rutile TiO_2 are obtainable. This prepared sulfated titania showed high catalytic activity in direct amidation of fatty acids as well as benzoic acids with various amines under solvent-free conditions.



INTRODUCTION

Amide bond linkage is a worldwide and important core structure in pharmaceutical, chemical, and many natural products.[1] Many procedures for the formation of amides are known in the literature.[2] The most common methods are the reaction between carboxylic acid derivatives particularly acid halides, acid anhydrides, and esters with the amines. Despite their wide scope, limitations are associated with the use of acid halides, anhydrides, and esters. Limitations are mostly due to the limited stability of many acid chlorides and the need for preparation of hazardous reagents (thionyl chlorides, etc.), which release corrosive and volatile byproducts. Reactions with esters require strongly basic or acidic catalysts.[3] Thus, the reaction between carboxylic acids and amines for the preparation of amides is preferred.

Fatty acid amides are of considerable interest due to their wide rang of application in lubricants, surfactants, cosmetics, shampoo, detergents, photographic materials, polyolefin foaming materials, polymer stabilizers, photocurable developers, and pigments.[4−10] Fatty acid amides have been prepared by reaction of fatty acids with anhydrous ammonia under high temperature (200 °C) and high pressure.[11] In this procedure, an additional purification step is also required to obtain pure fatty amide. To overcome these drawbacks, enzymatic synthesis offers potential alternative processes.[12−15] However, in their preparation procedures, primary fatty amides such as oleamide from oleic acid and erucamide from erucic acid have been prepared as the main products.

Recently, Sharma,[16a] Khare,[16b] and co-workers reported that synthesis of bioactive *N*-alkyl fatty amide derivatives using enzymes as catalyst. Terada[16c] and co-workers have also developed metal salts as versatile catalysts for amidation of fatty acids.

Therefore, amidation of fatty acids imparts a broad spectrum of activity against bacteria, yeasts, and molds.[17] Due to enhanced functionality and significant bioactive properties in secondary fatty amides, there is an increasing interest in their production and characterization. Thus, a need to develop new methods for environmentally friendly amidation is substantial.

In recent years, solid catalysts have been of considerable interest because of their advantages such as nonhazardous nature, selectivity, requirement in catalytic amounts, and easier reaction workup. The ease of separation and option of reusability of the solid catalysts render the process as green. Among the various solid catalysts, sulfated metal oxides are potential catalysts for many reactions. Sulfated titania has been proven one of the most useful sulfated metal oxides.

In this paper, as a part of our continuing research works on nano metal oxides catalysts,[18] we report the preparation of a new nano-sized sulfated titania by a sol−gel method that have a large specific surface area ~218 $m^2\ g^{-1}$. Furthermore, the catalytic activity of nano sulfated titania was applied to effective synthesis of fatty amides in the absence of any coupling reagents and solvents.

RESULTS AND DISCUSSION

X-ray Diffraction (XRD) Analysis. Figure 1 shows the XRD pattern of nano sulfated TiO_2. Combination of both phases' rutile TiO_2 and anatase TiO_2 morphologies are clearly shown according to the XRD pattern. The peaks positioned at $2\theta = 25^o$, 32^o, and 38^o are related to the (110), (101), and (111) of rutile TiO_2, respectively, whereas the peaks situated at $2\theta = 48^o$ and 72^o belong to the (211) and (220) phases of the anatase TiO_2 structure.[19] The average crystallite size was determined using the Scherrer equation.[20] Therefore, in accordance with the XRD pattern, it is clearly implied that the proposed procedure majored to the formation of both morphologies including rutile and anatase TiO_2.

SEM and TEM. The size and structure of the sulfated TiO_2 were also evaluated using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). According to the

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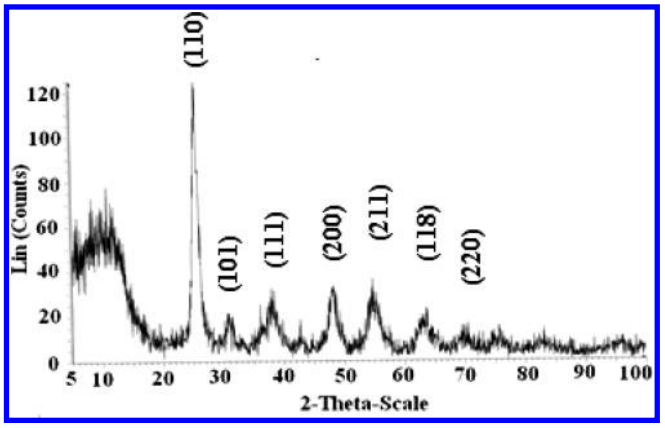

Figure 1. XRD pattern of nano sulfated TiO_2.

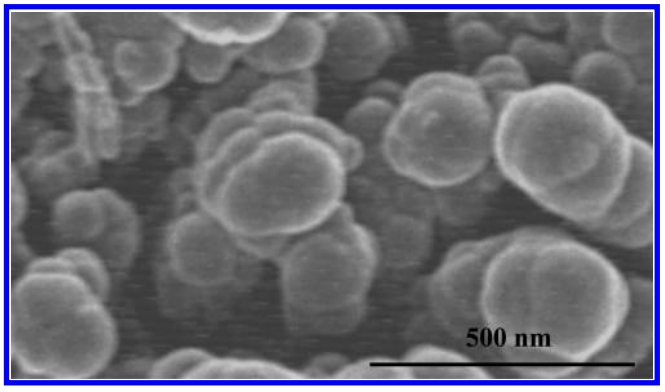

Figure 2. SEM image of nano sulfated TiO_2.

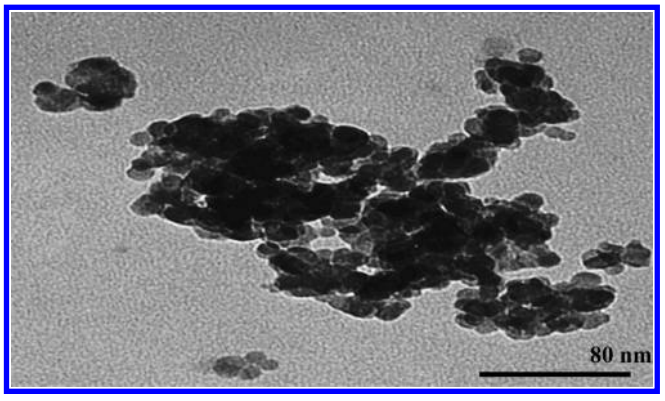

Figure 3. TEM image of nano sulfated TiO_2.

SEM (Figure 2) and TEM (Figure 3), it was observed that the synthesized sulfated TiO_2 catalyst have nano dimension ranging from ~40 to 250 nm. It was also observed that, during the sulfonation of TiO_2, some of TiO_2 morphologies are partially aggregated with each other, resulting in the formation of larger clusters of TiO_2 nano particles.

FT-IR Spectroscopy and Thermogravimetric Analysis. In this work, FT-IR spectroscopy is adopted as an applicable technique for further characterization of the sulfated TiO_2. The IR spectrum of TiO2 has been reported in the literature, and two well-defined bands at 646 and 552 cm^{-1} were attributed to TiO_2

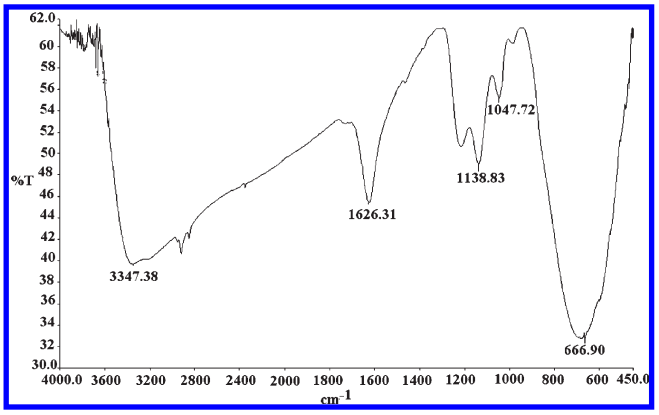

Figure 4. FT-IR spectrum of nano sulfated TiO_2.

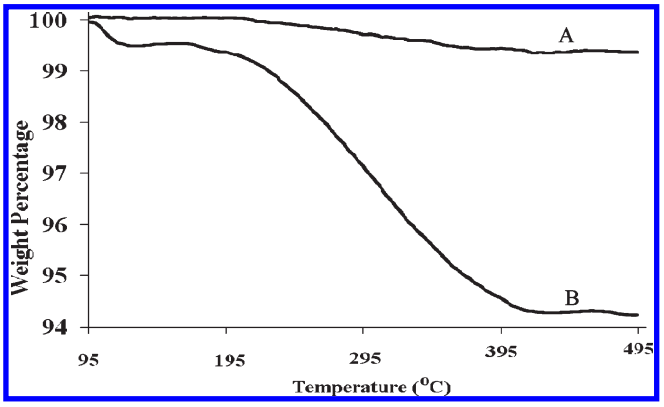

Figure 5. Thermograms revealing the thermal stability of (A) pure TiO_2 and (B) sulfated TiO_2.

in the rutile form.[21] This presence of a well-defined band positioned at 666.90 cm^{-1} is quite evident, which is related to the formation of TiO_2 in rutile morphology (see Figure 4). On the basis of the literature,[21] the absorbance bands related to the Ti−O stretching and Ti−O−Ti bending characterize the formation of the anatase structure of TiO_2. In this study according to the FT-IR spectrum (Figure 4) only a broad absorbance band positioned at 666.90 cm^{-1} reveals the formation of TiO_2 in both rutile and anatase forms. This result is in accord with that obtained from the XRD studies. Also, the peaks positioned at 1047.72 and 1138.83 cm^{-1} are related to stretching of the S═O band.[22] It should be noted that one band at 1626.31 cm^{-1}, belongs to H−O−H bending during the adsorption of water molecules. In addition, the strong peak at 3347.38 cm^{-1} is due to the stretching of OH groups caused during the adsorption of water.[23] In this study, the adsorption of water molecules was shown using thermogravimetric (TG) analysis.

The thermal behavior of nano sulfated TiO_2 and pure TiO_2 is shown in Figure 5. A significant decrease in the weight percentage of the sulfated TiO_2 at about ~100 °C is related to desorption of water molecules from the catalyst substrate. This was evaluated to ~0.7% according to the TG analysis. In addition, the sharp decrease in the weight percentage at temperature around 290 °C is due to the decomposition of sulfuric acid and formation of sulfur dioxide. According to the thermogram, the amount of sulfuric acid functionalized on TiO_2 support is evaluated to be ~5.8% (w/w).

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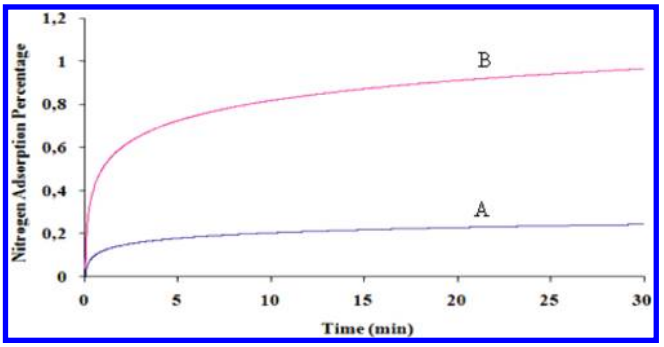
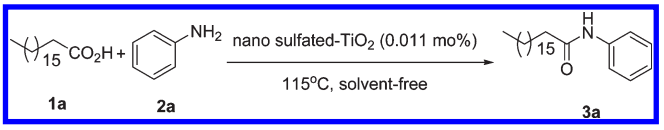


Figure 6. Nitrogen adsorption isotherms of (A) pure TiO_2 and (B) sulfated TiO_2.

Scheme 1



From further analysis of the synthesized catalyst, the value of pH of sulfated TiO_2 emulsion was studied. For this purpose, the same amounts of pure TiO_2 or sulfated TiO_2 (~0.02 g) were sonicated inside two separated bottles containing 5.0 mL H_2O. Under similar conditions, it was observed that there is a significant difference in the pH. This difference was evaluated to ~5.13 pH units, revealing the capability of the synthesized catalyst to act as a suitable proton-donating agent during the synthesis of organic compounds.

Nitrogen Adsorption Isotherm. The N_2 adsorption isotherms of the synthesized sulfated TiO_2 and pure TiO_2 at 25 °C using a homemade TG analysis system are shown in Figure 6. In accordance with the N_2 adsorption isotherms, significant increase to ~0.8% was evaluated for TiO_2 during the sulfate process. According to the N_2 adsorption isotherms, there is a significant increase to ~218 $m^2 g^{-1}$ in the active surface area of the TiO_2 during the sulfate process.

Catalytic Activity of the Nano Sulfated TiO_2 for Amidation of Carboxylic Acids. The main objective of the present work is to investigate and characterize the activity of nano sulfated TiO_2 as the heterogeneous catalyst for direct amidation of carboxylic acids. So far, it was tested as catalyst for the amidation of fatty acids. To find out the activity of nano sulfated TiO_2 as a general amidation catalyst, we chose stearic acid **1a** as a representative substrate and treated **1a** with aniline **2a** under solvent-free conditions. The amidation of **1a** was completed in 3 h at 115 °C by using a catalytic amount of nano sulfated TiO_2 (0.011 mo%) to give stearamide **3a** in 98% yield (Scheme 1).

Performing the experiment in the absence of nano sulfated TiO_2 did not lead to any products even after 48 h. On the other hand, this catalyst lost its efficiency in the presence of organic solvents such as ethanol, acetonitrile, toluene, chloroform, dichloromethane, and water. This observation gives the impression that the solvent-free condition plays an important role in this reaction.

To establish the general applicability of nano sulfated TiO_2 as an amidation catalyst, a wide range of anilines containing various electron-donating and -withdrawing groups and primary and secondary aliphatic amines were treated with an equimolar amount of stearic acid (Table 1). Excellent results were obtained in each case affording the corresponding amide derivatives in 70−98% yields in 3−12 h at 115 °C under solvent-free conditions.

As shown in Table 1, various aromatic and aliphatic amine as well as heterocyclic and ambidentate amines react with stearic acid to give the corresponding amides in good to high yields. In most cases, the product obtained after the usual workup was pure (spectral data), without requiring additional efforts of purification. Wherever required, the purification was performed by column chromatography.

Moreover, the mildness/efficiency and chemoselectivity of the nano sulfated TiO_2 were demonstrated with heteroaromatic and aromatic diamines (entries 7, 8) that resulted in the formation of the corresponding mono amide in excellent yield. It is interesting to note that in the case of the amines **2g** and **2h** when we used 2 equiv of amines in the reaction conditions, selectively the corresponding mono amides **3g** and **3h** were obtained in the same yield, without any side product.

In the case of amidation of morpholine with stearic acid, the corresponding amide was obtained in a yield higher than that reported by Taddei et al.[24] by using solid supported chloro-[1,3,5]triazine as catalyst. It is interesting to note that fatty acid amides plasticizers have shown that the morpholides of fatty acids such as oleic acid and stearic acids are compatible and efficient plasticizers for homo- and copolymers of vinyl chloride.[25]

Recently *N*-alkyl fatty acid amides have assumed great important,[26] so we planned to investigate the application of nano sulfated TiO_2 catalyst for synthesis of *N*-alkyl fatty amides. The amidation of fatty amines such as dodecyl amine and hexadecyl amine was performed with stearic acid using nano sulfated TiO_2 as catalyst. The amidation proceeded efficiently for both fatty amines, resulting in the formation of corresponding fatty acid amides in high yield (98%) (entries 12, 13). Nanosulfated TiO_2 gave amides in high yields irrespective of the chain length of fatty amine. These tendencies are different from recent reports that the catalytic activity of various catalyst changed with the changing of the chain length of amines.[27]

In addition, caprylic and lauric acids were also reacted with aniline to form the corresponding amides in the same reaction conditions. In both cases the corresponding amides obtained in high yields (98%) after 3 h (Scheme 2).

In order to investigate and generalize the reaction condition, we then chose a range of aromatic carboxylic acids in the amidation reaction using nano sulfated titania under the same reaction conditions (Scheme 3). The results are shown in Table 2.

In conclusion, the production of *N*-alkyl fatty acid amides from the amidation of stearic acid, caprylic acid, and lauric acid with various amines using nano sulfated TiO_2 as a catalyst was investigated in the present study. The nano sulfated TiO_2 was obtained by sol−gel methodology and characterized in terms of its acidity and structural aspects. Also, this catalyst is very active in the amidation of fatty acids and also aromatic/aliphatic carboxylic acids with various amines. The advantages are as follows: (a) the use of a cheap and easily prepared catalyst, (b) solvent-free conditions, (c) short reaction times and high yields, (d) easy reaction procedure and workup, (e) use of very low catalytic amount of catalyst (0.011 mol %), and (f) stoichiometric amounts of both components (acid and amine) in order to avoid environmental waste and fulfill the philosophy of green chemistry.[28]

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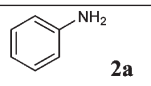
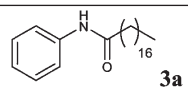
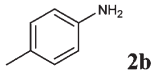
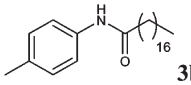
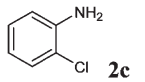
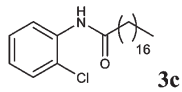
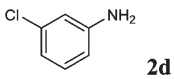
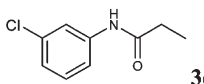
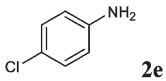
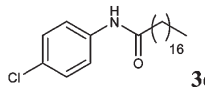
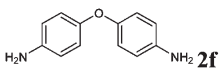
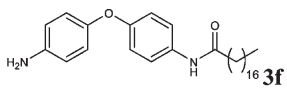
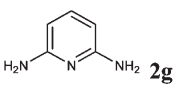
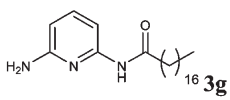
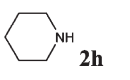
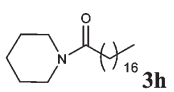
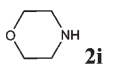
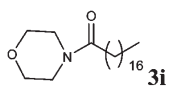
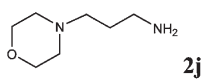
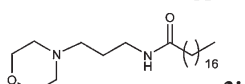
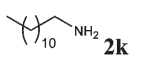
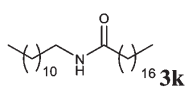
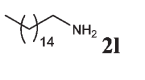
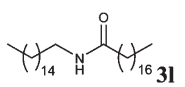
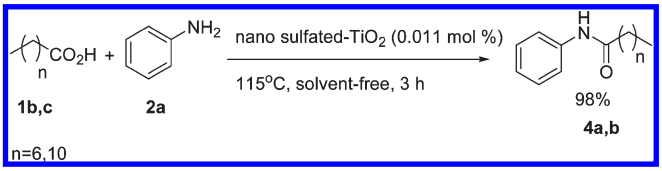
Table 1. Direct Amidation of Various Amines (2) with Stearic Acid 1a Catalyzed by Nano Sulfated TiO_2[a]

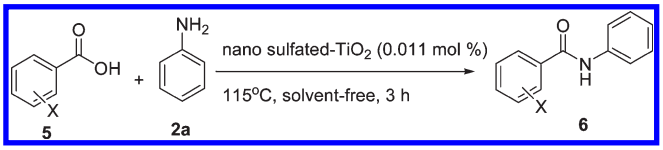
Entry	Amine	Amide	Time (h)	Yield(%)[b]
1	 **2a**	 **3a**	3	98
2	 **2b**	 **3b**	2.5	98
3	 **2c**	 **3c**	9	98
4	 **2d**	 **3d**	6.5	98
5	 **2e**	 **3e**	5.5	98
6	 **2f**	 **3f**	12	70
7	 **2g**	 **3g**	6	50
8	 **2h**	 **3h**	12	70
9	 **2i**	 **3i**	2.5	95
10	 **2j**	 **3j**	1	98
11	 **2k**	 **3k**	2.5	98
12	 **2l**	 **3l**	2.5	98

[a] Reaction conditions: stearic acid (1.0 mmol), amine (1.0 mmol), catalyst (0.011 mol %), in an oil bath at 115 °C. [b] Isolated yield.

Scheme 2



Scheme 3



EXPERIMENTAL SECTION

Materials and Instruments for Preparation and Characterization of the Catalyst. Titanium isobutoxide ($C_{16}H_{36}O_4Ti$) was purchased from Fluka Company. Power X-ray diffraction (XRD) was performed on a Bruker D8-advance X-ray diffractometer with Cu Kα (λ = 1.54178 Å) radiation. The morphology of the products were determined by using Leica Cambridge, model s360, version V03.03 Scanning electron microscopy (SEM) performed at accelerating voltage of 25 Kv. The size of the nano flakes was confirmed by a Philips CM10 TEM instrument.

Catalyst Preparation. Sulfated TiO_2 nano powder was prepared by a sol−gel process. Titanium isobutoxide (98% Fluka) was used as the source of TiO_2. A 14.3 mL portion of Ti $(OC_4H_9)_4$ was hydrolyzed in 150 mL of water containing 1.25 mL of nitric acid (65% Merck), and then the aqueous solution was stirred continuously at room temperature for 2 h to form a highly dispersed sol, which was concentrated and dried at 60 °C. Sulfation was done using 0.5 M sulfuric acid solution (2.0 g mL^{-1}). The samples, after 2 h of drying at 110 °C, were calcined for 5 h at 500 °C.

Amidation of Carboxylic Acids with Amines. Amidation reaction was performed in a flux at atmospheric pressure equipped with

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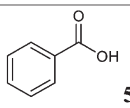
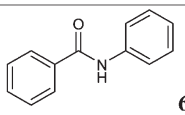
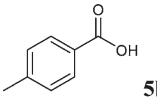
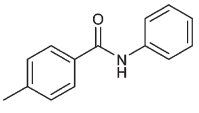
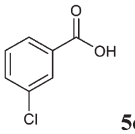
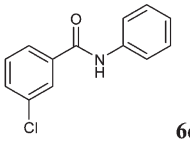
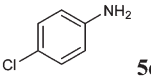
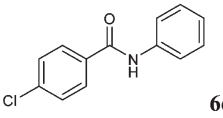
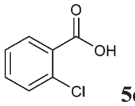
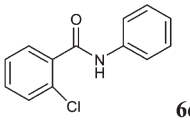
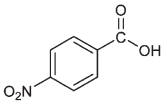
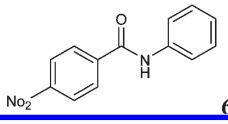
Table 2. Direct Amidation of Various Carboxylic Acids with Aniline Catalyzed by Nano Sulfated TiO_2[a]

Entry	Acid	Amide	Time (h)	Yield (%)[b]
1	 **5a**	 **6a**	2.5	95
2	 **5b**	 **6b**	3	95
3	 **5c**	 **6c**	3.5	98
4	 **5d**	 **6d**	4	98
5	 **5e**	 **6e**	6	95
6	 **5f**	 **6f**	4.5	95

[a] Reaction conditions: benzoic acids (1.0 mmol), aniline (1.0 mmol), in an oil bath at 115 °C. [b] Isolated yield.

a Teflon-coated magnetic stir bar. A mixture of carboxylic acid (1.0 mmol), amine (1.0 mmol), and nano sulfated TiO_2 (0.2 g, 0.011 mol %) was stirred magnetically at 115 °C and 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 × 10 mL) and water (3 × 10 mL) to afford the crude product, which was dried over $CaCl_2$ and concentrated by rotary vacuum evaporation. Further purification was performed by column chromatography using petroleum ether and EtOAc as solvent to yield the expected products. All products were characterized by NMR, IR, mass spectra, and CHN analysis data, which for known compounds were found to be identical with the literature and only ^1H and ^{13}C NMR. The complete spectroscopic data are described in Supporting Information.

***N*-Phenyl Stearamide (3a).** White solid; mp 85−87 °C; ^1H NMR (250 MHz, $CDCl_3$) δ 0.85 (3H, t, J = 6.59 Hz), 1.25 (28H, m), 1.69−1.71 (2H, m), 2.21 (2H, t, J = 7.46 Hz), 7.09 (1H, m), 7.26 (1H, s), 7.33 (2H, m), 7.50−7.53 (2H, m); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 14.1, 22.7, 25.5, 29.3, 29.4, 29.5, 29.7, 31.9, 37.8, 119.8, 124.1, 128.9, 138.7, 173.5 some peaks were overlapped; IR cm^{-1} (KBr) 1657, 2912, 3342; MS m/z (%) 359 (0.4) [M^+]. Anal. Calcd for molecular formula $C_{24}H_{41}NO$: C, 80.16; H, 11.49%. Found: C, 80.02, H, 11.33%.

***N*-*P*-Tolyl stearamide (3b)[29].** White solid; mp 70−71 °C; ^1H NMR (250 MHz, $CDCl_3$) δ 0.88 (3H, t, J = 6.92 Hz), 1.25 (28H, m), 1.68−1.74 (2H, m), 2.30 (3H, s), 2.33 (2H, t, J = 7.54 Hz), 7.11 (2H, d, J = 8.17 Hz), 7.26 (1H, s), 7.39 (2H, d, J = 8.30 Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 14.1, 20.8, 22.7, 25.7, 29.3, 29.4, 29.5, 29.6, 29.6, 29.7, 31.9, 37.8, 119.9, 129.4, 135.0, 173.0 some peaks were overlapped.

***N*-(2-Chlorophenyl) Stearamide (3c)[29].** White solid; mp 68−70 °C; ^1H NMR (250 MHz, $CDCl_3$) δ 0.87 (3H, t, J = 6.30 Hz), 1.25 (28H, m), 1.62−1.73 (2H, m), 2.3 (2H, t, J = 7.42 Hz), 6.98−7.04 (1H, m), 7.20−7.35 (2H, m), 7.68 (1H, s), 8.37 (1H, d, J = 8.05 Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 14.1, 22.7, 24.7, 24.9, 25.5, 27.9, 29.1, 29.2, 29.3, 29.4, 29.4, 29.5, 29.5, 29.6, 29.7, 31.9, 37.9, 121.8, 122.7, 124.5, 127.6, 128.9, 134.5, 171.6.

***N*-(3-Chlorophenyl) Stearamide (3d)[29].** White solid; mp 51−53 °C; 1H NMR (250 MHz, $CDCl_3$) δ 0.87 (3H, t, J = 6.30 Hz), 1.25 (28H, m), 1.62−1.73 (2H, m), 2.3 (2H, t, J = 7.42 Hz), 7.04 (1H, m), 7.22−7.28 (2H, m), 7.37 (1H, d, J = 8.05 Hz), 7.64 (1H, s); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 14.1, 22.7, 25.6, 29.3, 29.4, 29.4, 29.5, 29.6, 29.7, 29.7, 31.9, 37.7, 117.9, 120.1, 124.2, 129.8, 134.5, 139.2, 172.1 some peaks were overlapped.

***N*-(4-Clorophenyl) Stearamide (3e)[29].** White solid; mp 56−58 °C; ^1H NMR (250 MHz, $CDCl_3$) δ 0.86 (3H, t, J = 6.86 Hz), 1.25 (28H, m), 1.47 (2H, m), 2.18 (2H, t, J = 7.40 Hz), 7.24 (1H, d, J = 8.83 Hz), 7.38 (1H, s), 7.45 (1H, d, J = 8.89 Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 14.1, 22.7, 25.5, 29.2, 29.4, 29.5, 29.6, 29.7, 31.9, 37.7, 120.9, 128.9, 136.6, 173.1 some peaks were overlapped.

***N*-(4-(4-Aminophenoxy)phenyl) Stearamide (3f)[30].** Yellow solid; mp 116−118 °C; ^1H NMR (250 MHz, DMSO-d_6) δ 0.82 (3H, t, J = 6.75 Hz), 1.20 28H, m), 1.46−1.53 (2H, m), 2.3 (2H, t, J = 7.20 Hz), 5.10 (1H, s), 6.56 (2H, d, J = 7.73 Hz), 6.69 (2H, d, J = 7.67 Hz), 6.77 (2H, d, J = 7.98 Hz), 7.47 (2H, d, J = 8.81 Hz), 9.74 (2H, s); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 14.1, 22.7, 24.9, 25.4, 29.2, 29.4, 29.5, 29.7, 31.9,

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34.4, 37.5, 103.3, 104.2, 141.5, 149.2, 156.0, 172.5 some peaks were overlapped.

***N*-(6-Aminopyridin-2-yl) Stearamide (3g).** White solid; mp 70.5−72 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.62 (3H, t, J = 6.00 Hz), 0.99 (28 H, m), 1.35−1.44 (2H, m), 2.09 (2H, t, J = 7.32 Hz), 4.36 (2H, s), 5.96 (2H, d, J = 7.92 Hz), 7.13−7.32 (1H, m), 8.94 (1H, s); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 14.1, 22.7, 25.4, 27.9, 29.3, 31.9, 34.7, 37.5, 140.6, 149.8, 156.8, 172.2 some peaks were overlapped; IR cm^{-1} (KBr) 1667, 2912, 3310.60, 3495.20; MS m/z (%) 375 (0.10) [M$^+$]. Anal. Calcd for molecular formula $C_{23}H_{41}N_3O$: C, 73.55; H, 11.00%. Found: C, 73.46, H, 10.97%.

1-(Piperidin-1-yl) Octadeca-1-one (3h). Viscose liquid; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.86 (3H, t, J = 6.03 Hz), 1.24 (28 H, m), 1.55−1.60 (8 H, m), 2.31 (2H, t, J = 7.14 Hz), 3.46 (4H, m); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 14.1, 22.7, 24.5, 24.8, 25.5, 26.1, 29.1, 29.3, 29.4, 29.5, 29.7, 31.9, 33.4, 33.9, 171.5 some peaks were overlapped; IR cm^{-1} (KBr) 1644.70, 2923.40, 3456; MS m/z (%) 351 (0.90) [M$^+$]. Anal. Calcd for molecular formula $C_{23}H_{45}NO$: C, 78.57; H, 12.90%. Found: C, 78.69; H, 12.84%.

1-Morpholineooctadeca-1-one (3i). White solid; mp 42−44 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.84 (3H, t, J = 6.17 Hz), 1.22 (28 H, m), 1.57−1.62 (2H, m), 2.29 (2H, t, J = 7.36 Hz), 3.44 (4H, m), 3.62−3.64 (4H, m); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 14.1, 22.7, 24.8, 25.3, 29.1, 29.3, 29.3, 29.4, 29.4, 29.5, 29.6, 29.6, 29.7, 29.9, 31.9, 33.1, 34.0, 41.8, 46.1, 66.8, 172.1 some peaks were overlapped; IR cm^{-1} (KBr) 1628, 2922, 3457; MS m/z (%) 353 (0.80) [M$^+$]. Anal. Calcd for molecular formula $C_{22}H_{43}NO_2$: C, 74.73; H, 12.26%. Found: C, 74.68; H, 12.20%.

***N*-(3-Morpholinopropyl) Stearamide (3j).** White solid; mp 59−61 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.85 (3H, t, J = 6.39 Hz), 1.22 (28H, m), 1.59−1.68 (4H, m), 2.14 (2H, t, J = 7.16 Hz), 2.42 (6H, m), 3.33 (2H, t, J = 6.80 Hz), 3.67−3.69 (4H, m), 6.29 (1H, s); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 14.1, 22.6, 24.9, 25.2, 25.9, 29.3, 29.4, 29.5, 29.7, 31.9, 34.8, 36.9, 38.9, 53.5, 57.5, 66.7, 173.1 some peaks were overlapped; IR cm^{-1} (KBr) 1638, 2923, 3331; MS m/z (%) 411 (2.4) [M$^+$+1]. Anal. Calcd for molecular formula $C_{25}H_{50}N_2O_2$: C, 73.12; H, 12.27%. Found: C, 73.07; H, 12.21%.

***N*-Dodecyl Stearamide (3k).** Brown solid; mp 90−91 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.63 (6H, t, J = 6.99 Hz), 0.99 (46H, m), 1.22−1.32 (4H, m), 1.93 (2H, t, J = 7.35 Hz), 2.60 (2H, t, J = 7.48 Hz), 5.40 (1H, s); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 14.1, 22.7, 24.7, 25.8, 26.9, 29.1, 29.3, 29.3, 29.4, 29.4, 29.5, 29.6, 29.7, 31.9, 34.1, 36.9, 39.5, 173.4 some peaks were overlapped; IR cm^{-1} (KBr) 1633, 2912, 3320; MS m/z (%) 451 (5.8) [M$^+$]. Anal. Calcd for molecular formula $C_{30}H_{61}NO$: C, 79.75; H, 13.61%. Found: C, 79.70; H, 13.58%.

***N*-Hexadecyl Stearamide (3l).** Brown solid; mp 98−100 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.63 (6H, t, J = 6.99 Hz), 1.23 (56H, m), 1.37 (4H, m), 2.07 (2H, t, J = 7.35 Hz), 2.99 (2H, t, J = 7.48 Hz), 5.32 (1H, s); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 14.1, 22.7, 24.7, 25.8, 26.9, 28.1, 29.1, 29.3, 29.4, 29.5, 29.7, 31.9, 33.9, 39.5, 173.4 some peaks were overlapped ; IR cm^{-1} (KBr) 1638, 2912, 3331; MS m/z (%) 506 (3) [M$^+$−1]. Anal. Calcd for molecular formula $C_{34}H_{69}NO$: C, 80.40; H, 13.69%. Found: C, 80.36; H, 13.57%.

***N*-Phenyl Octanamide (4a).** White solid; mp 82−84 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.88 (3H, t, J = 6.46 Hz), 1.26 (10H, m), 2.24 (2H, t, J = 7.46 Hz), 7.15 (1H, m), 7.32 (1H, s), 7.43−7.52 (2H, m), 7.63 (2H, d, J = 8.21 Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 14.0, 22.6, 24.9, 29.1, 31.6, 34.4, 119.8, 124.1, 128.9, 138.5, 173.3 some peaks were overlapped; IR cm^{-1} (KBr) 1655, 2917, 3337; MS m/z (%) 219 (12) [M$^+$]. Anal. Calcd for molecular formula $C_{14}H_{21}NO$: C, 76.67; H, 9.65%. Found: C, 76.61, H, 9.53%.

***N*-Phenyl Dodecanamide (4b).** White solid; mp 93−86 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.71 (3H, t, J = 6.07 Hz), 0.95 (18H, m), 1.99 (2H, t, J = 7.48 Hz), 7.07 (1H, m), 7.36 (1H, s), 7.46−7.60 (2H, m), 7.72 (2H, d, J = 8.40 Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 13.8, 22.5, 24.8, 28.7, 29.0, 29.5, 29.8, 31.8, 36.1, 173.4 some peaks were overlapped; IR cm^{-1} (KBr) 1656, 2912, 3331; MS m/z (%) 275 (1.9) [M$^+$]. Anal. Calcd for molecular formula $C_{18}H_{29}NO$: C, 78.49; H, 10.61%. Found: C, 78.40, H, 10.54%.

***N*-Phenyl Benzamide (6a)[31].** White solid; mp 162−164 °C (lit.[35] 162−163 °C); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.33−7.43 (3H, m), 7.49−7.54 (3H, m), 7.65 (2H, d, J = 8.17 Hz), 7.85 (2H, d, J = 8.30 Hz), 7.87 (1H, s); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 120.3, 124.6, 127.1, 128.7, 129.1, 131.8, 134.9, 137.9, 165.9 some peaks were overlapped.

4-Methyl-*N*-phenyl Benzamide (6b)[31]. White solid; mp 155−157 °C (lit.[36] 149−150 °C) ; ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.43 (s, 3H), 7.22 (2H, d, J = 8.17 Hz), 7.35−7.52 (5H, m), 7.78 (2H, d, J = 8.30 Hz), 7.93 (1H, s); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 23.2, 120.4, 127.6, 128.9, 129.5, 131.5, 134.5, 135.9, 134.0, 165.9 some peaks were overlapped.

3-Chloro-*N*-phenyl Benzamide (6c)[32]. White solid; mp 186−188 °C (lit.[32] 187−188 °C) ; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.11−7.20 (2H, m), 7.24−7.35 (2H, m), 7.39 (1H, m), 7.53 (1H, d, J = 8.01 Hz), 7.65 (2H, d, J = 8.40 Hz), 7.87 (1H, d, J = 8.14 Hz), 7.94 (1H, s), 8.06 (1H, s); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 121.4, 124.4, 125.8, 127.5, 129.0, 130.2, 132.5, 134.1, 135.9, 135.9, 164.6 some peaks were overlapped.

4-Chloro-*N*-phenyl Benzamide (6d)[33]. White solid; mp 201−202 °C (lit.[36] 195−196 °C); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.34 (2H, d, J = 8.20 Hz), 7.42−7.59 (5H, m), 7.82 (2H, d, J = 8.14 Hz), 7.95 (1H, s); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 121.6, 124.3, 128.9, 129.2, 129.2, 132.1, 135.9, 137.7, 165.3 some peaks were overlapped.

2-Chloro-*N*-phenyl Benzamide (6e)[34]. White solid; mp 184−186 °C (lit.[34] 180−182 °C); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.13−7.19 (1H, m), 7.32−7.39 (3H, m), 7.56 (2H, m), 7.73 (2H, d, J = 8.32 Hz), 7.85 (1H, d, J = 8.45 Hz), 8.24 (1H, s); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 120.9, 124.4, 127.1, 128.9, 129.0, 132.6, 132.7, 134.1, 136.3, 165.8 some peaks were overlapped.

4-Nitro-*N*-phenyl Benzamide (6f)[33]. Pale yellow solid; mp 198−199 °C (lit.[36] 217−218 °C); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.55 (2H, d, J = 8.23 Hz), 7.58−7.65 (5H, m), 7.74 (2H, d, J = 8.14 Hz), 7.90 (1H, s); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 121.3, 121.7, 124.5, 128.6, 129.1, 135.8, 140.2, 151.7, 164.9 some peaks were overlapped.

■ ASSOCIATED CONTENT

Supporting Information. Experimental procedures, spectroscopic data for all compounds, and ^{1}H NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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