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Chitosan-Silica Sulfate Nano Hybrid (CSSNH) as a Novel and Highly Proficient Heterogeneous Nano Catalyst for Regioselective Ring Opening of Epoxides via Carboxylic Acids

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The synthesis and characterization of chitosan-silica sulfate nano hybrid (CSSNH) as a novel and efficient heterogeneous nano catalyst involving acid-base bifunctional activity is described. The catalytic potency and activity of this eco-friendly catalyst was investigated in regioselective ring opening of epoxides with carboxylic acids to access structurally diverse 1,2-diol mono-esters in good to excellent yields. CSSNH catalyst was characterized using different microscopic and spectroscopic techniques encompassing scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), N2 adsorption isotherm, and Fourier transform infrared spectroscopy (FT-IR). The green nature, cheapness, efficiency, ease of preparation, handling and reusability of this new catalyst makes this catalyst to be useful for green industrial processes.

Keywords: carboxylic acid • CSSNH • epoxide • heterogeneous catalyst • nano hybrid

Introduction

Epoxides as a carbon-electrophile play a significant role in organic synthesis due to their facile ring opening reaction with vary nucleophiles [1]. In this regard, epoxides are extensively used for preparation of numerous 1,2-difunctional compounds [2]. Although the ring opening reaction of epoxides via diverse nucleophiles has been widely studied; however, there has been little attention

to the ring opening of epoxides with carboxylic acids. The ring opening of epoxides with carboxylic acids is a well-known strategy to obtain 1,2-diol mono-esters (β-hydroxy esters) as useful precursors applied in production of surfactants especially for oil and gas industries [3], synthesis of biocompatible and biodegradable polymers [4], biolubricants [5,6], fragrances and pharmaceuticals [7,8]. Additionally, 1,2-diol mono-esters are valuable intermediates used in the total synthesis of steroids and carbohydrates [9,10].

The ring opening reaction of epoxides with carboxylic acids are generally carried out under different conditions including acidic, basic and neutral conditions [11]. However, most of the reported methods suffer from one or more drawbacks such as harsh reaction condition, high catalyst loading, low conversion and moderate yield, limited substrate scope, the use of expensive reagents or catalysts, and finally the use of non-reusable and/or non-recyclable catalysts. In this context, the search for a mild, green, and low-cost protocol for facile and efficient ring opening of epoxides with carboxylic acids is still desired.

In recent decades, acid-base dual-activation which enables the cooperative activation of both reactants has been the subject of considerable research interest since it mimics the enzymatic process in nature [12]. This protocol is of great significance for efficient progress of nucleophilic reactions under mild and convenient conditions. The dual-activation strategies generally include, (*i*) the use of two separate catalysts and/or reagents, (*ii*) the use of one molecule having two separate active cores as a bifunctional catalyst and/or reagent, and (*iii*) the use of one catalyst in which merely activates one reactant and subsequently, the *in situ* generated reactive substrate that can promote the activation of the other reactants [13-16]. The ring opening reaction of epoxides with different nucleophiles using dual-activation catalysts is well established [12, 17-19]. In this context, the acid-base dual-activation strategy has been successfully employed for the ring opening of epoxides with carboxylic acids using $FeCl_3$/Et_3N and/or *N*-methylmorpholine [20] and also $FeCl_3$/pyridine [21] in homogeneous conditions.

Nowadays, the use of heterogeneous catalysts in organic reactions is highly preferred to homogeneous catalysts owing to both environmental and economic aspects. In particular, there has been a growing interest in the application of natural biopolymers as environmentally benign materials for preparation of heterogeneous catalysts [22,23]. Along this line, polysaccharides as one of the most abundant biomolecules in nature are extensively applied. Among polysaccharides, chitosan (CS, Figure 1) has gained tremendous research interest due to its unique properties such as biocompatibility and biodegradability, non-toxicity, inertness towards air and moisture, hydrophilicity, chemical reactivity, excellent chelating ability, and the ease of chemical modification owing to presence of hydroxyl and amino functionalities [24-26]. Chitosan is utilized as environmental friendly material since it can be readily degraded by water and soil microorganisms. In addition, chitosan is a very cheap natural biopolymer present in industrial waste and also easily can be acquired by alkaline deacetylation of chitin from crustacean [27]. Thus, an increasing industrial and scientific interest has been focused on the application of chitosan in different fields such as pharmaceutical, drug delivery, cosmetics, food packaging, adhesives, waste water treatment, membranes, surface conditioners, hydrogels, and fuel cells [28-30]. Aside from the extensive utilization of chitosan as a biopolymer support for the synthesis of heterogeneous catalysts [31-37], it can be efficiently used as the heterogeneous catalyst in its parental shape without any post-modification [38-40].

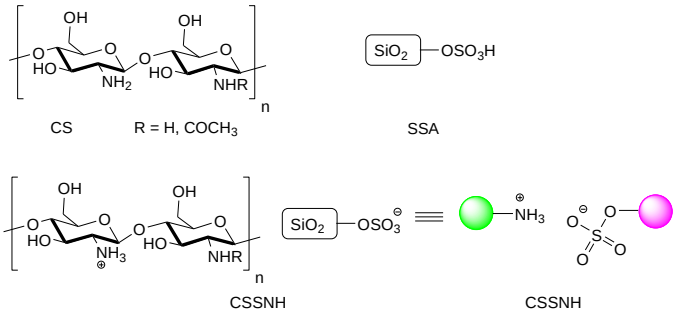
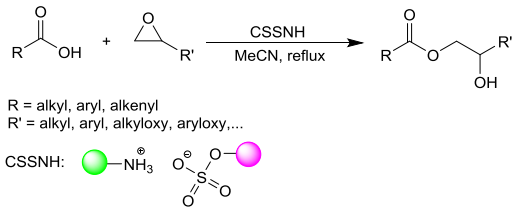


Figure 1. The general structure of chitosan (CS), silica sulfuric acid (SSA) and chitosan-silica sulfate nano hybrid (CSSNH).

In recent years, organic-inorganic hybrid materials or catalysts have gained particular attention [41]. Regarding to the benefits of biopolymers as the green catalysts, the use of biopolymer-inorganic hybrid catalysts has been emerged as an attractive strategy in preparation of new catalysts in organic reactions. In this context, there have been several reports on immobilization of chitosan or chitosan-metal complexes on the surface of porous silica gel [42]. In most cases, the utilization of these hybrid catalysts have been reported in oxidation and hydrogenation reactions, asymmetric dihydroxylation of olefins, and carbonylation reactions [42]. Molvinger and co-workers have reported the application of chitosan-silica hybrid in reaction of lauric acid with glycidol [43].

Silica sulfuric acid (SSA, Figure 1) is an eco-friendly heterogeneous acid catalyst derived from silica gel which successfully applied in numerous organic transformations [44]. However, to the best of our knowledge, there have been no reports yet on synthesis and application of chitosan-silica sulfate nano hybrid (CSSNH) material as a green and economical organic-inorganic hybrid catalyst. In light of the advantages of organic-inorganic hybrid catalysts and also inspired by the acid-base dual-activation strategy, hereby we describe the synthesis and characterization of chitosan-silica sulfate nano hybrid (CSSNH) as a novel, environmental benign, and low-cost bifunctional heterogeneous nano catalyst. The catalytic activity of this new biodegradable catalyst was investigated in the synthesis of 1,2-diol mono-esters via regioselective ring opening reaction of epoxides with structurally diverse carboxylic acids in MeCN at reflux condition (Scheme 1).



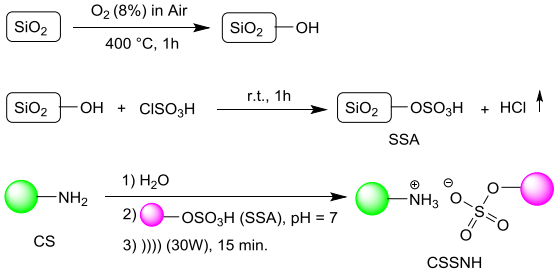
Scheme 1. Synthesis of 1,2-diol mono-esters via ring opening reaction of epoxides with carboxylic acids using chitosan-silica sulfate nano hybrid (CSSNH).

Results and Discussion

Preparation of CSSNH

The process for the preparation of CSSNH is shown in Scheme 2. The first step of the catalyst synthesis was initiated by preparing SSA. Due to our previous experience, the better result was obtained when the activated SiO_2 was applied instead of ordinary SiO_2 to react with $ClSO_3H$ [45]. Thus, the exposure of normal silica with a flow of 8% O_2 in an argon atmosphere was achieved for 1h at 400 °C in a furnace. Then, $ClSO_3H$ (0.02 mol per 6.0 g silica) was added dropwise to the activated silica followed by stirring the reaction mixture for 1h at room temperature. To prepare CSSNH, chitosan was then added to an open-capped cylindrical pyrex-glass containing demineralized water.

Subsequently, freshly prepared SSA was added portionwise to the mixture. When the pH of the reaction mixture was reached to 7, the mixture was exposed to ultrasonic irradiation (30W) for 15 min. Filtration followed by drying provided CSSNH hybrid catalyst as a creamy solid (Figure 2).

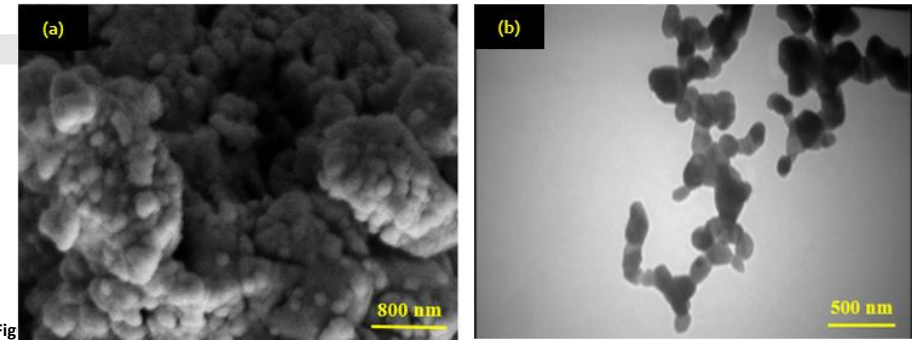


Scheme 2. Preparation of chitosan-silica sulfate nano hybrid (CSSNH).

Fig sulfate nano hybrid.

Characterization of the catalyst nanostructure

The obtained CSSNH catalyst was characterized by various techniques involving scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), nitrogen adsorption isotherm, and Fourier transform infrared spectroscopy (FT-IR). Figure 3 shows the SEM and TEM images of CSSNH catalyst, respectively.



Fig

The distribution of particle size for CSSNH catalyst has been indicated by corresponding TEM and SEM images. As it can be seen in Figure 4, about 45% of total CSSNH nanoparticles have size around 90 nm that clearly endorses the efficiency of applied procedure for synthesizing CSSNH as a green nano-catalyst.

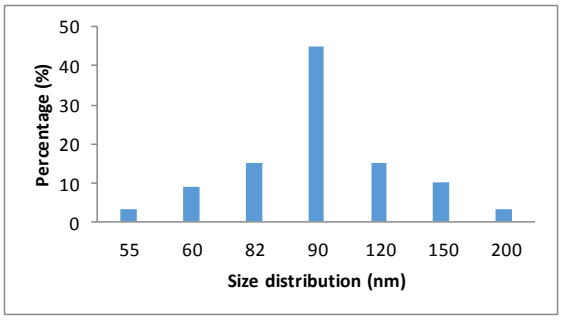


Figure4. Histogram showing size distribution of chitosan-silica sulfate nano hybrid (CSSNH).

The Si morphology of CSSNH has also been characterized by patterned XRD as shown in Figure 5. As clearly shown, the diffractions positioned at 2θ equal to 25 and 48° are assigned to Si morphology.

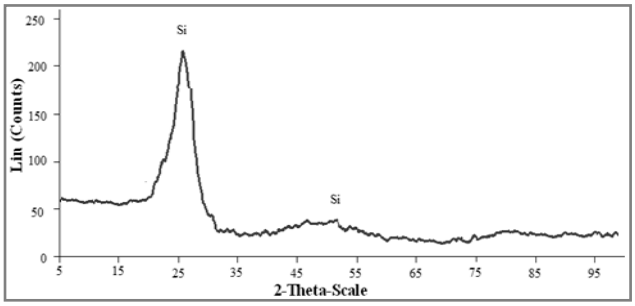


Figure 5. XRD pattern of chitosan-silica sulfate nano hybrid (CSSNH).

The nitrogen adsorption isotherm of CSSNH has also been shown in Figure 6. Based on the results, compared to the silica powder as the adopted precursor, significant enhancement around 73 $m^2 g^{-1}$ was observed in the active surface during immobilization of chitosan.

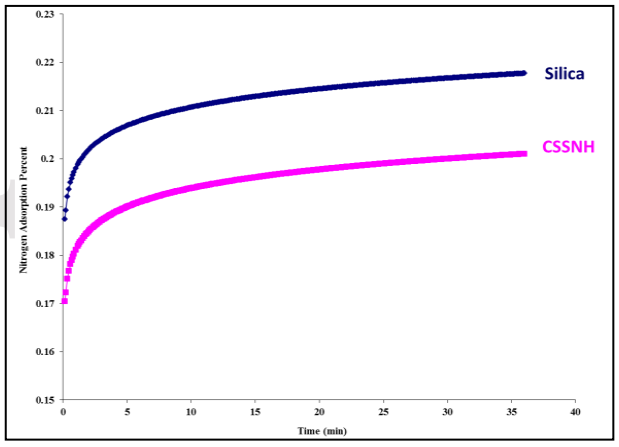


Figure 6. N_2 adsorption isotherms of chitosan-silica sulfate nano hybrid (CSSNH).

The comparison between FT-IR spectra of CSSNH catalyst, CS and SSA is shown in Figure 7. The FT-IR spectrum of chitosan shows a broad band at 3407 cm^{-1} which corresponds to the stretching vibrations of O–H and N–H groups. The band at 2891 cm^{-1} displays the stretching vibrations of the C–H bond. The absorption band present at 1568 cm^{-1} corresponds to the N–H bending vibration. The bands around 1391 cm^{-1} are assigned to symmetric bending vibration of CH. The band at 1053 cm^{-1} indicates the stretching vibrations of the C–O bond. The FT-IR spectrum of SSA displays a band at 780

cm^{-1} which is due to S–O stretching. A broad peak at 1007–1213 cm^{-1} is related to the stretching symmetric and anti-symmetric Si–O–Si, symmetric and asymmetric stretching of O=S=O bonds. The broad band at 3479 cm^{-1} is assigned to the stretching vibration of different hydroxyl moieties. The FT-IR spectrum pattern of CSSNH catalyst displays a different fingerprint region at 400–1520 cm^{-1} in comparison with that of pure chitosan which indicates a decisive interaction between chitosan and SSA. Apparently, the peak at 1568 cm^{-1} is shifted to 1520 cm^{-1} after treating of chitosan with SSA. In addition, the intensity of shifted N–H bending vibration at 1520 cm^{-1} is decreased which is due to the protonated amino groups present in the synthesized catalyst.

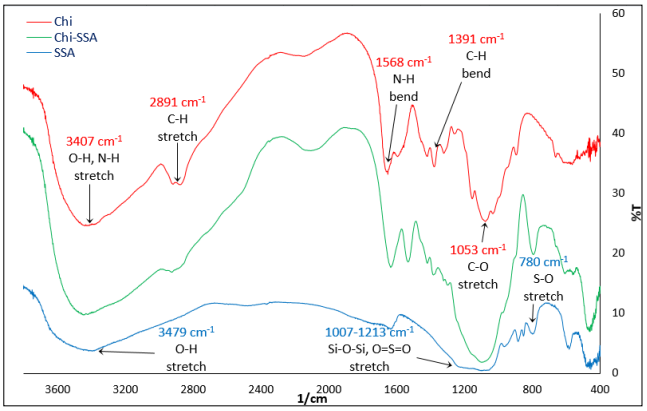


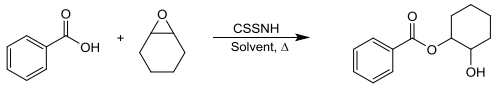
Figure 7. The FT-IR spectrum of CS, SSA, and CSSNH catalyst.

Application of CSSNH catalyst in ring opening of epoxides via carboxylic acids

After synthesis and characterization of CSSNH catalyst then it was applied in synthesis of structurally diverse 1,2-diol mono-esters via regioselective ring opening reaction of epoxides with carboxylic acids. Initially, efforts have been focused on optimizing the reaction conditions. To this end, the reaction of cyclohexene oxide with benzoic acid in the presence of CSSNH catalyst was selected as the sample reaction to afford 2-hydroxycyclohexyl benzoate. Thus, the influence of several effective factors on the reaction progress including solvent type, temperature, and catalyst amount was studied in preparing 2-hydroxycyclohexyl benzoate.

In this concern, to indicate the significance of solvent, the sample reaction was carried out under solvent-free conditions. However, the desired product was obtained in low yield even if the reaction time was prolonged up to 18h (Table 1, entry 1). Thus, we screened the effect of various protic and aprotic solvents on progress of the sample reaction (Table 1).

Table 1. The influence of various solvents and temperatures on sample reaction using CSSNH catalyst [a].



Entry	Solvent	Temperature (°C)	Time (h)	Yield [b] (%)
1	solvent-free [c]	100	18	12
2	H_2O	r.t.	24	NR [d]
3	H_2O	40	18	trace
4	H_2O	60	18	20
5	H_2O	80	15	26
6	H_2O	90	15	32
7	H_2O	reflux	10	36
8	DMSO	100	8	57
9	DMF	100	8	60
10	acetone	reflux	12	45
11	$CHCl_3$	reflux	14	28
12	toluene	reflux	10	30
13	MeCN	reflux	4	96
14	MeCN	r.t.	18	trace
15	MeCN	50	10	45
16	MeCN	60	9	70
17	MeCN	70	6	89
18	MeCN	95 [c]	4	96

[a] Reaction conditions: benzoic acid (1 mmol), cyclohexene oxide (1.2 mmol), CSSNH catalyst (0.03 g), solvent (5 mL). [b] Isolated yield. [c] The reaction was tested in a sealed tube. [d] No reaction.

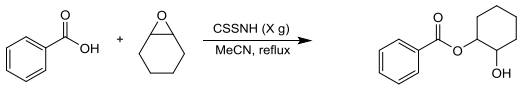
As the results in Table 1 indicate, the solvent type has a substantial role in progress of the reaction. Since the green nature of water, the use of this solvent in organic reactions has been an important subject of many research interests. Hence, the sample reaction was examined in an aquatic media at ambient temperature; however, no product was observed even in a trace amount (Table 1, entry 2). To improve the reaction efficiency, the effect of different temperatures was studied on the sample reaction when water was used as the solvent. As can be seen in Table 1, increasing the reaction temperature affects the reaction progress to some extent (entries 2-7). In addition, when the reaction was performed in refluxing water, the desired 1,2-diol mono-ester was obtained in 36%

yield after 10h (entry 7). Thus, we focused on the use of several traditional organic solvents (Table 1). As shown in Table 1, when the sample reaction was tested in DMSO or DMF (entries 8 and 9) the moderate yields of product were obtained. The use of acetone, $CHCl_3$, and toluene affords the product in low yields (entries 10-12). Moreover, the use of MeCN led to desire product in a shorter reaction time (Table 1, entry 13). Hence, MeCN was selected as the solvent of choice for all subsequent reactions.

In another experiment, the influence of vary temperatures on progress of the sample reaction in MeCN was studied (Table 1, entries 13-18). The obtained results indicate that increasing the reaction temperature can effectively accelerate the reaction rate and improve the yield. Practically, the higher yield of the product in a shorter reaction time was acquired when the sample reaction was performed in refluxing MeCN (Table 1, entry 13). In addition, more elevation in temperature provided no distinguishable raise on reaction progress (Table 1, entry 18).

The catalyst loading is another important parameter in upgrading the ring opening reaction of epoxides with carboxylic acids (Table 2). Apparently, in the absence of the catalyst, a very low yield of product (<10%) was obtained (Table 2, entry 1). As shown in Table 2, the higher yield and rate of sample reaction was gained when it was carried out in the presence of 0.03 g CSSNH catalyst (Table 2, entry 4). The reasonable yields of sample product were also afforded using lower amount of catalyst when the reaction time was prolonged up to 7h (Table 2, entries 2 and 3). No further improvement was observed when the catalyst amount was raised from 0.03 g up to 0.05 g (Table 2, entries 5 and 6).

Table 2. Effect of various amounts of CSSNH on sample reaction [a].



Entry	X g CSSNH	Time (h)	Yield [b] (%)
1	0	10	trace
2	0.01	7	80
3	0.02	7	89
4	0.03	4	96
5	0.04	4	96
6	0.05	4	95

[a] Reaction conditions: benzoic acid (1 mmol), cyclohexene oxide (1.2 mmol), CSSNH (X g), solvent (5 mL). [b] Isolated yield.

To prove the catalytic potency of CSSNH in ring opening reaction of epoxides with carboxylic acids, we carried out the sample reaction in the presence of CS and/or SSA alone under the optimized conditions. Practically, performing the sample reaction under the optimized conditions using CSSNH led to 2-hydroxycyclohexyl benzoate in 96% yield after 4 h. However, using CS and SSA as the reaction catalyst under the optimized reaction conditions affords the corresponding product in 47% and 23% yields after 4 h, respectively. These results indicate that neither CS nor SSA were as efficient as CSSNH for progress of the reaction.

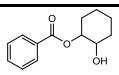
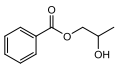
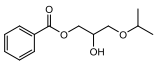
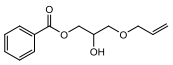
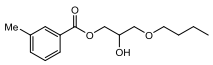
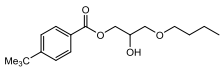
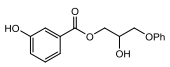
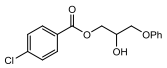
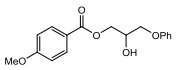
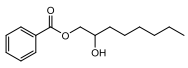
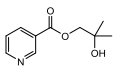
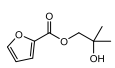
Having optimized the reaction conditions, we then explored the versatility and scope of current protocol in ring opening reaction of structurally diverse epoxides and carboxylic acids (Table 3). It is clear from Table 3 that CSSNH is a highly efficient and suitable heterogeneous nano catalyst for regioselective ring opening of different epoxides with various carboxylic acids. The generality of this protocol was confirmed with respect to aromatic (Table 3, entries 1-10), heteroaromatic (Table 3, entries 11 and 12), vinylic (Table 3, entry

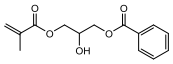
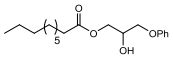
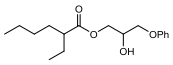
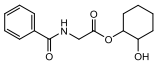
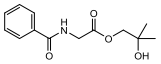
13) and long chain aliphatic carboxylic acids (Table 3, entries 14 and 15). Additionally, the *N*-protected amino acids can be successfully applied in this protocol to provide the desired 1,2-diol mono-esters in excellent yields (Table 3, entry 16 and 17).

The chemoselectivity of the present method was assessed by its application for 3-hydroxyl benzoic acid (Table 3, entry 7). As shown in Table 3, the corresponding 1,2-diol mono-ester was obtained in 92% yield as the sole product and the phenolic OH residue did not interfere in the ring opening reaction of epoxide. Also, the method works well with structurally diverse epoxides involving terminal and vicinal epoxides using CSSNH catalyst.

We further explored the capability of the present protocol for a large scale synthesis. To this end, the sample reaction was carried out on a 100 mmol scale under the optimized reaction conditions which led to the formation of 2-hydroxycyclohexyl benzoate in 90% yield.

Table 3. Synthesis of 1,2-diol mono-esters using CSSNH catalyst.

Entry	Product a	Time (h)	Yield b (%)
1		4	96
2		4	92
3		4	93
4		4	95
5		5	90
6		5	87
7		4	92
8		4.5	90
9		4	95
10		4.5	92
11		6	89
12		4	91

13		5	93
14		4	95
15		4	92
16		6	91
17		6	94

[a] All products were characterized by ^{1}H and ^{13}C NMR, IR, CHN, and MS analysis. [b] Isolated yield.

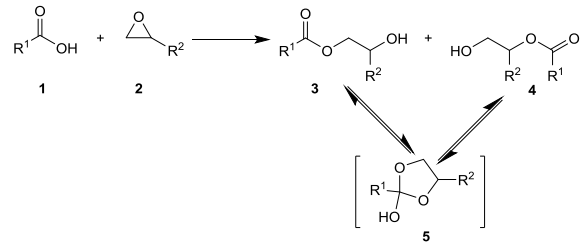
The recyclability and reusability of the catalyst is a significant task as an evidence for its heterogeneous nature. Hence, the recoverability and reusability of CSSNH catalyst was explored under the optimized conditions. In this context, after completion of the reaction, the catalyst was recovered and dried. Then, it was directly applied in subsequent reaction while no fresh catalyst was added to the reaction mixture. The obtained results demonstrated that CSSNH catalyst is a recoverable and reusable catalyst which can be efficiently employed for at least 6 consecutive runs without significant decline in its activity (Table 4).

Table 4. The reusability of CSSNH catalyst [a].

Run number [b]	Time (h)	Yield [c] (%)
1	4	96
2	4	96
3	4	94
4	5	93
5	5	92
6	6	91

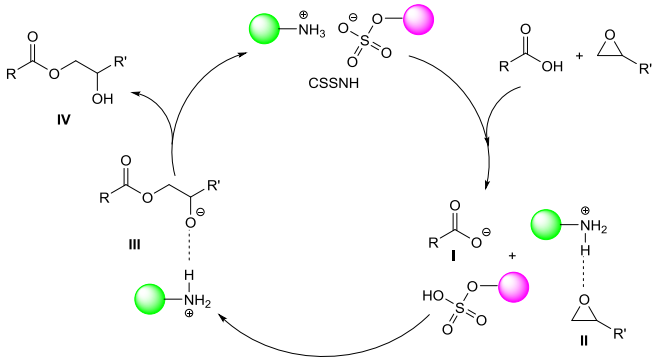
[a] Reaction conditions: benzoic acid (1 mmol), cyclohexene oxide (1.2 mmol), CSSNH catalyst, MeCN (5 mL). [b] The entry number corresponds to the trial number. [c] Isolated yield.

The ring opening reaction of epoxide with carboxylic acid generally produces two regioisomers **3** and **4** (Scheme 3). Under mild conditions, the reaction is achieved through the regioselective attack of carboxylic acid to less hindered side of epoxide to afford product **3**. However, product **4** can also be obtained in harsh reaction conditions through nucleophilic attack to the more hindered carbon. Moreover, it is well-indicated that the acyl migration of 1,2-diol mono-esters (i.e. isomerization) can be happened through a five-membered ring intermediate **5** (Scheme 3) [46,47]. Thus, product **4** can be also produced through the acyl transfer of initially generated **3**. However, the ring opening of epoxides with carboxylic acids was regioselectively achieved using the current catalyst in which majorly led to isomers **3** in good to excellent yields. The regioisomers **4** were also obtained in trace amounts.



Scheme 3. Isomerization of 1,2-diol mono-esters.

A plausible mechanism is suggested to explain the acid-base dual-activation role of CSSNH in catalyzing the ring opening reaction of epoxides with carboxylic acids (Scheme 4). As shown in Scheme 4, silica sulfate anion acts as the base and deprotonates the carboxylic acid to produce the carboxylate anion **I**. On the other hand, protonated chitosan acts as the acid and interacts with epoxide oxygen (adduct **II**) for activating the epoxide to undergo the nucleophilic attack. Then, treatment of **I** with **II** affords adduct **III**. Eventually, protonolysis of adduct **III** generates the desired 1,2-diol mono-ester **IV** and librates the catalyst.



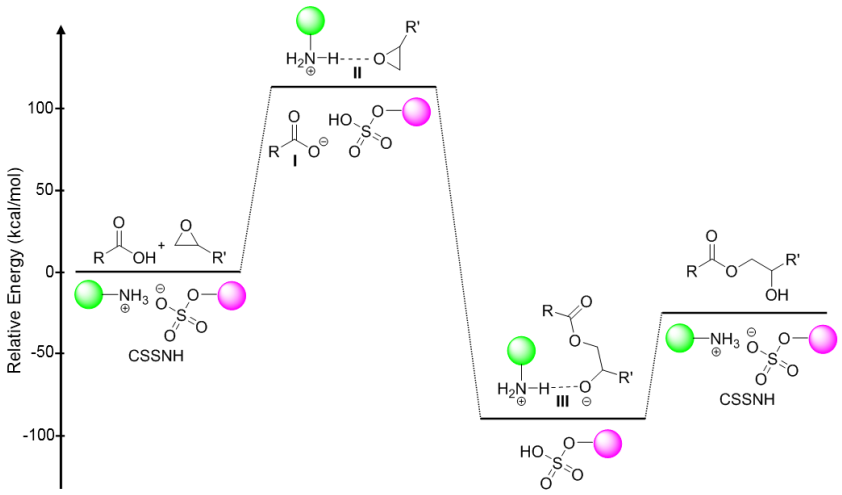
Scheme 4. A plausible reaction mechanism.

Using quantum chemical calculations, the full optimization of epoxide, carboxylic acid, CSSNH catalyst, anion **I**, adduct **II**, adduct **III**, SSA, SSA anion, chitosan cation and product were performed by Gaussian 09 software [48]. In our calculations, benzoic acid (Scheme 4, R= Ph) and 2-methyloxirane (Scheme 4, R'= Me) were applied as the model compounds. All calculations were carried out by density functional theory (DFT) on the B3LYP/6-31+G(d,p) level of theory, containing polarizable and diffuse functions. The interaction energy (DE) was estimated by employing the counterpoise (CP) method for the Gaussian basis set superposition error (BSSE) [49]. The results confirm the formation of a relatively strong H-bond with 10.74 kcal/mol energy and 1.77 Å distance between oxygen atom of epoxide and NH of chitosan residue (adduct **II**). This interaction plays a critical role for activation the epoxide toward the nucleophilic attack. In the last step, the proton transfers from the NH of chitosan residue to the oxygen anion in adduct **III** which led to the formation of 1,2-diol mono-ester **IV** and recycling the CSSNH catalyst. Table 5 shows the total (Hartree) and relative (kcal/mol) energies of optimized structure for the ring opening reaction of 2-methyloxirane with benzoic acid in the presence of CSSNH. The reaction energy diagram for the proposed mechanism is depicted in Figure 8.

Table 5. The total and relative energies of optimized structure for the reaction between 2-methyloxirane and benzoic acid using CSSNH [a].

Optimized geometry	Total energies (Hartree)	Relative energies (kcal/mol)
Epoxide+Carboxylic acid+CSSNH	-4336.21530	0.00
Anion **I**+ Adduct **II**+SSA	-4336.03574	112.67
Adduct **III**+SSA	-4336.35742	-89.18
Product **IV**+SSA	-4336.25434	-24.50

[a] All calculations were performed using DFT on the B3LYP/6-31+G(d,p) level of theory



Conclusions

In summary, we have explained the synthesis, characterization and application of CSSNH as a new, green, non-toxic, and inexpensive heterogeneous nano catalyst with dual mode of action. The bifunctional activity of CSSNH catalyst was successfully applied in synthesis of 1,2-diol mono-esters via regioselective ring opening of epoxides with carboxylic acids. The advantages of this approach involve the green nature and reusability of the catalyst, high efficiency, mild reaction condition, low catalyst loading, ease of operation, as well as applicability in large scale synthesis. Owing to numerous benefits acquired by utilizing CSSNH, the expansion of other applications of this catalyst in organic transformations is the subject of our future attempts.

Experimental Section

All chemical reagents were purchased from Fluka, Merck or Sigma-Aldrich. Solvents were purified by standard procedures, and stored over 3Å molecular sieves. Reactions were followed by TLC using SILG/UV 254 silica-gel plates. Column chromatography was performed on silica gel 60 (0.063-0.200 mm, 70-230 mesh; ASTM). Melting points were measured using Electrothermal IA 9000 melting point

apparatus in open capillary tubes and are uncorrected. IR spectra were obtained using a Shimadzu FT-IR-8300 spectrophotometer. Ultrasonication was performed using a horn sonicator, Misonix model S-4000 (Qsonica LLC, Newtown, CT.) with a standard titanium tip diameters of ½". The transmission electron microscopy was employed using TEM (CN-10, Philips, 100 KV). The scanning electron micrograph was attained using SEM (XL-30 FEG, Philips, 20 KV) instrument. The patterned X-ray diffraction (XRD) was obtained using D8 Advance, Brüker AXS. The nitrogen adsorption isotherm was achieved on lab-made Metrohm instrument. ^{1}H- and ^{13}C-NMR spectrum was recorded on Brüker Avance-DPX-250/400 spectrometer operating at 250/62.5 MHz, respectively. Chemical shifts are given in δ relative to tetramethylsilane (TMS) as an internal standard, coupling constants *J* are given in Hz. GC/MS was performed on a Shimadzu GC/MS-QP 1000-EX apparatus (m/z; rel.%). Elemental analyses were performed on a Perkin–Elmer 240-B micro-analyser.

General procedure for synthesis of SSA [45]

Activation of silica gel: In a tubing thermal furnace (internal diameter: 2.0 cm, length: 25 cm), a sample of normal silica gel (12.0 g) was exposed to a flow of 8% O_2 in an argon atmosphere for 1 h at 400 °C in which afforded the activated silica gel.

Synthesis of SSA: In a 50 mL suction flask containing activated silica gel (6.0 g) equipped with a gas inlet tube and a constant-pressure dropping funnel, was added dropwise $ClSO_3H$ (0.02 mol per 6.0 g silica gel) using the dropping funnel over a period of 1 h at room temperature followed by stirring the reaction mixture . The *in situ* generated HCl gas was absorbed over cold H_2O through the gas inlet tube. After complete addition of $ClSO_3H$ to the reaction mixture, the mixture was stirred for additional 30 min. SSA (7.6 g) was obtained as a white solid which was directly used in the next step.

General procedure for synthesis of CSSNH

In an open-capped cylindrical pyrex-glass (50 mL), was added chitosan (1 g, medium molecular weight, Aldrich, CAS No: 9012-76-4) in demineralized water (10 ml). Then, pH of the mixture was reduced to 7 by adding SSA (0.5 g). The mixture was kept at room temperature and irradiated at 30W power (cup horn: 20 kHz) in ultrasonic apparatus for 15 min. Afterward, the catalyst was filtered off and dried in a vacuum oven at 50 C for 2 h and stored in a sealed vessel at refrigerator.

General procedure for synthesis of 1,2-diol mono-esters using CSSNH catalyst

To a round bottom flask (50 mL) was added a mixture of appropriate carboxylic acid (1 mmol), epoxide (1.2 mmol), and CSSNH (0.03 g) in MeCN (5 mL). The reaction mixture was refluxed until TLC monitoring indicated no further improvement in the conversion (Table 3). Afterward, the catalyst was filtered off and washed with hot MeCN. The filtrate was evaporated to remove the solvent. Then, water (15 mL) was added to the remaining foam and it was subsequently washed with $CHCl_3$ (2 × 10 mL). The organic layer was dried (Na_2SO_4) and evaporated. The crude product was purified by column chromatography on silica gel eluting with a mixture of *n*-hexane/EtOAc.

Recycling the catalyst

After completion of the reaction as indicated by TLC monitoring (Table 3), the catalyst was vacuum-filtered from the reaction mixture using a sintered glass funnel and washed with MeCN (2 × 2 mL). Subsequently, the catalyst was kept in a vacuum oven at 50 °C for 2h. The recovered catalyst was then applied in next reaction without further purification.

2-Hydroxycyclohexyl Benzoate (entry **1**).

Column chromatography purification on silica gel with *n*-hexane-EtOAc (5:2) gave white crystals (0.21 g, 96%); mp 104-105 ºC; R_f 0.73 (50% *n*-hexane-EtOAc). IR (KBr): 3600-3100 (br), 3050, 2985, 1730, 1260 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ_{ppm} = 8.00-7.20 (m, 5 H, aryl), 4.80-4.76 (m, 1 H, $PhCO_2CH$), 3.68-3.64 (m, 1 H, *H*COH), 2.26 (s, 1 H, OH, exchangeable with D_2O), 2.10-1.26 (m, 8 H, $(CH_2)_4$). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ_{ppm} = 165.98, 133.54, 130.19, 129.59, 128.78, 80.43, 75.44, 30.79, 30.48, 23.80, 23.69. MS [m/z (%)]: 220.11 (9.1). Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.80; H, 7.37.

2-Hydroxypropyl Benzoate (entry **2**).

Column chromatography purification on silica gel with *n*-hexane-EtOAc (7:2) gave a colorless oil (0.16 g, 92%); R_f 0.54 (50% *n*-hexane-EtOAc). IR (liquid film): 3600-31500 (br), 3100, 2950, 1735, 1265 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ_{ppm} = 8.20-7.31 (m, 5 H, aryl), 4.53-4.42 (m, 1 H, $CH(OH)CH_3$), 4.42-4.21 (m, 2 H, $PhCO_2CH_2$), 2.34 (br s, 1 H, OH, exchangeable with D_2O), 1.38-1.22 (d, *J* = 5.9 Hz, 3 H, CH_3). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ_{ppm} = 167.24, 135.01, 134.98, 130.00, 127.63, 70.21, 66.20, 20.00. MS [m/z (%)]: 180.08 (7.9). Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.74; H, 6.78.

2-Hydroxy-3-(iso-propyloxy)propyl Benzoate (entry **3**).

Column chromatography purification on silica gel with *n*-hexane-EtOAc (5:2) gave a colorless oil (0.22 g, 93%); R_f 0.83 (50% *n*-hexane-EtOAc). IR (liquid film): 3600-3100 (br), 3050, 2980, 1735, 1265 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ_{ppm} = 8.24-7.28 (m, 5 H, aryl), 4.63-4.46 (dd, *J* = 2.6, 5.2 Hz, 2 H, $PhCO_2CH_2$), 4.26-4.00 (quint, *J* = 5.2, 1 H, *H*COH), 3.76-3.44 (m, 3 H, $(CH_3)_2CHO$, CH_2O(*iso*-Pr)), 3.33 (br s, 1 H, OH, exchangeable with D_2O),1.35-1.00 (d, *J* = 6.0 Hz, 6 H, 2 CH_3). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ_{ppm} = 163.71, 134.32, 131.36, 131.02, 127.64, 74.81, 70.33, 70.02, 66.32, 22.23. MS [m/z (%)]: 238.12 (10.5). Anal. Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.58; H, 7.69.

3-(Allyloxy)-2-hydroxypropyl Benzoate (entry **4**).

Column chromatography purification on silica gel elution with *n*-hexane-EtOAc (5:2) gave a colorless oil (0.22 g, 95%); R_f 0.60 (50% *n*-hexane-EtOAc). IR (liquid film): 3600-3150 (br), 3050, 2980, 1735, 1250 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ_{ppm} = 8.31-7.42 (m, 5 H, aryl), 6.00-5.72 (m, 1 H, $=CHCH_2$), 5.23-4.89 (dd, *J* = 10.4, 7.7 Hz, 2 H, $=CH_2$), 4.42-4.17 (d, *J* = 4.4 Hz, 2 H, $PhCO_2CH_2$), 4.11-4.00 (m, 1 H,

*H*COH), 4.00-3.81 (d, *J* = 5.5 Hz, 2 H, HCOHC*H*$_2$O), 3.50-3.38 (m, 2 H, =CHC*H*$_2$O), 2.76 (s, 1 H, OH, exchangeable with D_2O). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ_{ppm} = 167.22, 136.28, 135.01, 130.24, 129.62, 129.40, 117.28, 74.41, 71.22, 69.32, 65.13. MS [m/z (%)]: 236.26 (10.2). Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83. Found: C, 66.17; H, 6.92.

3-Butoxy-2-hydroxypropyl 3-methylbenzoate (entry **5**).

Column chromatography purification on silica gel elution with *n*-hexane-EtOAc (10:1) gave a yellow oil (0.24 g, 90%); R_f 0.91 (50% *n*-hexane-EtOAc). IR (liquid film): 3510-3190 (br), 3061, 2972, 1730, 1238 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ_{ppm} = 7.76-7.73 (m, 2 H, aryl), 7.27-7.17 (m, 2 H, aryl), 3.01 (s, 1 H, OH, exchangeable with D_2O), 4.33-4.27 (m, 2 H, CO_2CH_2), 4.05-4.03 (m, 1 H, *H*COH), 3.49-3.36 (m, 4 H, CH_2OCH_2), 2.28 (s, 3H, PhC*H*$_3$), 1.49-1.43 (m, 2 H, OCH_2CH_2), 1.31-1.22 (m, 2 H, C*H*$_2$CH$_3$), 0.78 (t, *J* = 7.3 Hz, 3 H, CH_2CH_3). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ_{ppm} = 164.92, 139.05, 133.43, 131.03, 130.75, 128.95, 126.90, 74.58, 71.33, 68.36, 67.15, 32.69, 24.10, 19.91, 14.30. MS [m/z (%)]: 266.15 (13.7). Anal. Calcd for $C_{15}H_{22}O_4$: C, 67.64; H, 8.33. Found: C, 67.51; H, 8.21.

3-Butoxy-2-hydroxypropyl 4-tert-butylbenzoate (entry **6**).

Column chromatography purification on silica gel elution with *n*-hexane-EtOAc (10:1) gave a yellow oil (0.27 g, 87%); R_f 0.92 (50% *n*-hexane-EtOAc). IR (liquid film): 3500-3200 (br), 3075, 2943, 1733, 1242 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ_{ppm} = 8.01-7.95 (m, 2 H, aryl), 7.47-7.43 (m, 2 H, aryl), 4.40-4.37 (m, 2 H, CO_2CH_2), 4.19-4.15 (m, 1 H, *H*COH), 3.57-3.46 (complex, 5 H, CH_2OCH_2, OH), 1.59-1.53 (m, 2 H, OCH_2CH_2), 1.41-1.33 (complex, 11 H, C*H*$_2$CH$_3$, C(CH$_3$)$_3$), 0.88 (t, *J* = 7.3 Hz, 3 H, CH_2CH_3). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ_{ppm} = 164.11, 154.68, 130.15, 127.74, 124.26, 74.78, 72.39, 69.45, 68.26, 41.02, 32.74, 30.96, 19.15, 14.97. MS [m/z (%)]: 308.20 (18.1). Anal. Calcd for $C_{18}H_{28}O_4$: C, 70.10; H, 9.15. Found: C, 70.19; H, 9.31.

2-Hydroxy-3-phenoxypropyl-3-hydroxy Benzoate (entry **7**).

Column chromatography purification on silica gel with *n*-hexane-EtOAc (5:3) gave pale yellow crystals (0.26 g, 92%); mp 63-65 ºC; R_f 0.53 (50% *n*-hexane-EtOAc). IR (KBr): 3600-3140 (br), 3100, 2980, 1730, 1250 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ_{ppm} = 7.86-6.93 (m, 9 H, aryl), 4.63-4.50 (dd, *J* = 2.2, 4.9 Hz, 2 H CO_2CH_2), 4.50-4.32 (quint, *J* = 4.9, 1 H, *H*COH), 4.29-4.00 (dd, *J* = 2.0, 4.9 Hz, 2 H, PhOC*H*$_2$), 4.00-3.00 (br s, 1 H, *H*OPh, exchangeable with D_2O), 2.50 (s, 1 H, OH, exchangeable with D_2O). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ_{ppm} = 167.33, 159.23, 156.31, 131.32, 130.29, 130.02, 123.62, 123.02, 122.07, 116.24, 115.00, 69.68, 69.41, 66.32. MS [m/z (%)]: 288.10 (12.5). Anal. Calcd for $C_{16}H_{16}O_5$: C, 66.66; H, 5.59. Found: C, 66.74; H, 5.48.

2-Hydroxy-3-phenoxypropyl-4-chloro Benzoate (entry **8**).

Column chromatography purification on silica gel elution with *n*-hexane-EtOAc (7:3) gave a colorless oil (0.28 g, 90%); R_f 0.73 (50% *n*-hexane-EtOAc). IR (liquid film): 3600-3150 (br), 3100, 2985, 1730, 1240 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ_{ppm} = 7.93-7.91 (d, *J* = 7.8 Hz, 2 H, aryl), 7.52-7.42 (d, *J* = 7.8 Hz, 2 H, aryl), 7.42-7.16 (m, 2 H, aryl), 7.16-6.83 (m, 3 H, aryl), 4.81-4.52 (dd, *J* = 4.9, 1.9 Hz, 2 H, *p*-$ClPhCO_2CH_2$), 4.42-4.38 (quint, *J* = 4.9, 1 H, *H*COH), 4.29-4.00 (dd, *J* = 4.9, 2.2 Hz, 2 H, CH_2OPh), 2.50 (s, 1 H, OH, exchangeable with D_2O). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ_{ppm} = 166.34, 158.24, 136.29, 132.67, 132.11, 130.44, 130.00, 126.68, 115.00, 69.36, 69.24, 65.98. MS [m/z (%)]: 306.07 (13.7). Anal. Calcd for $C_{16}H_{15}ClO_4$: C, 62.65; H, 4.93; Cl, 11.56. Found: C, 62.60; H, 5.02; Cl, 11.51.

2-Hydroxy-3-phenoxypropyl-4-methoxy Benzoate (entry **9**).

Column chromatography purification on silica gel with *n*-hexane-EtOAc (5:2) gave white crystals (0.29 g, 95%); mp 82-84 ºC; R_f 0.56 (50% *n*-hexane-EtOAc). IR (KBr): 3600-3150 (br), 3100, 2980, 1735, 1250 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ_{ppm} = 8.21-7.90 (d, *J* = 8.8 Hz, 2 H, aryl) 7.49-7.41 (d, *J* = 8.8 Hz, 2 H, aryl), 7.00-6.72 (m, 5H, aryl), 4.73-4.51 (dd, *J* = 1.9, 5.1 Hz, 2 H, *p*-$MeOPhCO_2CH_2$), 4.50-4.41 (quint, *J* = 5.1 Hz, 1 H, *H*COH), 4.39-4.21 (dd, *J* = 2.0, 5.1 Hz, 2 H, CH_2OPh), 3.90 (s, 3 H, OMe), 3.00 (s, 1 H, OH, exchangeable with D_2O). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ_{ppm} = 167.42, 165.00, 160.00, 133.64, 130.00, 123.62, 122.19, 115.00, 114.91, 70.26, 70.00, 65.00, 55.31. MS [m/z (%)]: 302.12 (11.7). Anal. Calcd for $C_{17}H_{18}O_5$: C, 67.54; H, 6.00. Found: C, 67.65; H, 6.14.

2-Hydroxyoctyl Benzoate (entry **10**).

Column chromatography purification on silica gel with *n*-hexane-EtOAc (7:2) gave white crystals (0.23 g, 92%); mp 48-50 ºC; R_f 0.81 (50% *n*-hexane-EtOAc). IR (KBr): 3600-3160 (br), 3100, 2980, 1730, 1250 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ_{ppm} = 8.25-7.32 (m, 5 H, aryl), 4.53-4.23 (m, 2 H, $PhCO_2CH_2$), 4.19-3.86 (m, 1 H, *H*COH), 2.45 (s, 1 H, OH, exchangeable with D_2O), 1.75-1.25 (m, 10 H, $(CH_2)_5$), 1.00-0.75 (t, *J* = 6.6 Hz, 3 H CH_3). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ_{ppm} = 167.24, 135.06, 130.09, 130.01, 127.68, 70.71, 69.11, 35.06, 32.71, 30.04, 25.22, 24.54, 15.10. MS [m/z (%)]: 250.16 (7.3). Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 72.05; H, 8.89.

2-Hydroxy-2-methylpropyl nicotinate (entry **11**).

Column chromatography purification on silica gel with *n*-hexane-EtOAc (1:1) gave brwon solid (0.17 g, 89%); mp 159-161 ºC; R_f 0.10 (50% *n*-hexane-EtOAc). IR (KBr): 350-3179 (br), 3040, 2972, 1734, 1235 cm^{-1}. ^1H NMR (250 MHz, DMSO-d_6): δ_{ppm} = 9.29 (s, 1 H, aryl), 9.00 (d, *J* = 7.6 Hz, 1 H, aryl), 8.87 (d, *J* = 7.6 Hz, 1 H, aryl), 8.14-8.09 (m, 1 H, aryl), 5.88 (s, 1 H, OH, exchangeable with D_2O), 4.71 (s, 2 H, CO_2CH_2), 1.17 (s, 6 H, 2 CH_3). ^{13}C NMR (62.5 MHz, DMSO-d_6): δ_{ppm} = 166.30, 152.04, 150.19, 136.83, 126.17, 122.53, 76.91, 68.73, 27.38. MS [m/z (%)]: 195.09 (10.4). Anal. Calcd for $C_{10}H_{13}NO_3$: C, 61.53; H, 6.71; N, 7.18. Found: C, 61.64; H, 6.86; N, 7.31.

2-Hydroxy-2-methylpropyl furan-2-carboxylate (entry **12**).

Column chromatography purification on silica gel with *n*-hexane-EtOAc (10:1) gave a brown oil (0.17 g, 91%); R_f 0.78 (50% *n*-hexane-EtOAc). IR (liquid film): 3500-3180 (br), 3064, 2987, 1732, 1240 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ_{ppm} = 7.61-7.59 (m, 1 H, C(5)-H, furan), 7.25-7.23 (m, 1 H, C(3)-H, furan), 6.53-6.50 (m, 1 H, C(4)-H, furan), 4.18 (s, 2 H, CO_2CH_2), 2.81 (s, 1 H, OH, exchangeable with D_2O), 1.29 (s, 6 H, 2 CH_3). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ_{ppm} = 159.74, 147.38, 144.97, 117.61, 112.18, 74.27, 67.34, 26.47. MS [m/z (%)]: 184.07 (9.5). Anal. Calcd for $C_9H_{12}O_4$: C, 58.69; H, 6.57. Found: C, 58.80; H, 6.71.

2-Hydroxy-3-(methacryloyloxy)propyl Benzoate (entry **13**).

Column chromatography purification on silica gel with *n*-hexane-EtOAc (5:3) gave a colorless oil (0.24 g, 93%); R_f 0.56 (50% *n*-hexane-EtOAc). IR (liquid film): 3600-3150 (br), 3050, 2980, 1730, 1720, 1250, 1230 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ_{ppm} = 8.41-7.36 (m, 5 H, aryl), 6.21 (s, 1 H, =C$H_a$$H_b$), 5.63 (s, 1 H, =$CH_a$$H_b$), 4.64-4.50 (m, 2 H, $PhCO_2CH_2$), 4.49-4.23 [m, 3 H, *H*CHOH, CH_2=C(Me)CO_2CH_2], 3.33 (br s, 1 H, OH, exchangeable with D_2O), 2.05 (s, 3 H, CH_3). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ_{ppm} = 167.21, 166.32, 136.22, 135.09, 130.06, 130.01, 128.51, 125.22, 69.90, 65.22, 65.09, 20.31. MS [m/z (%)]: 264.10 (8.7). Anal. Calcd for $C_{14}H_{16}O_5$: C, 63.63; H, 6.10. Found: C, 63.75; H, 6.14.

2-Hydroxy-3-phenoxypropyl decanoate (entry **14**).

Column chromatography purification on silica gel with *n*-hexane-EtOAc (10:1) gave a yellow oil (0.31 g, 95%); R_f 0.95 (50% *n*-hexane-EtOAc). IR (liquid film): 3530-3190 (br), 3050, 2973, 1735, 1248 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ_{ppm} = 7.31-7.24 (m, 2 H, aryl), 6.99-6.88 (m, 3 H, aryl), 4.31-4.12 (complex, 3 H, CO_2CH_2, *H*COH), 4.02-3.99 (m, 2 H, CH_2OPh), 2.88 (s, 1 H, OH, exchangeable with D_2O), 2.31 (t, *J* = 7.4 Hz, 2 H, CH_2CO_2), 1.64-1.56 (m, 2 H, C$H_2CH_2CO_2$), 1.32-1.25 (complex, 12 H, $CH_3(CH_2)_6$), 0.84 (t, *J* = 6.9 Hz, 3 H, CH_3). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ_{ppm} = 174.45, 156.38, 129.41, 120.53, 114.69, 70.24, 68.11, 67.91, 33.51, 31.96, 30.43, 29.81, 29.51, 29.22, 25.21, 22.46, 15.42. MS [m/z (%)]: 322.21 (18.6). Anal. Calcd for $C_{19}H_{30}O_4$: C, 70.77; H, 9.38. Found: C, 70.64; H, 9.27.

2-Hydroxy-3-phenoxypropyl 2-ethylhexanoate (entry **15**).

Column chromatography purification on silica gel with *n*-hexane-EtOAc (10:1) gave a colorless oil (0.27 g, 92%); R_f 0.95 (50% *n*-hexane-EtOAc). IR (liquid film): 3517-3194 (br), 3061, 2978, 1733, 1239 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ_{ppm} = 7.30-7.24 (m, 2 H, aryl), 6.98-6.88 (m, 3 H, aryl), 4.31-4.20 (complex, 3 H, CO_2CH_2, *H*COH), 4.02-3.99 (m, 2 H, CH_2OPh), 2.94 (s, 1 H, OH, exchangeable with D_2O), 2.32-2.29 (m, 1 H, $CHCO_2$), 1.63-1.49 (m, 4 H, (CH_2CH_2CH), 1.29-1.23 (m, 4 H, 2 C$H_2$$CH_3$), 0.91-0.83 (m, 6 H, 2 CH_3). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ_{ppm} = 174.82, 158.17, 129.74, 120.81, 115.20, 70.98, 69.19, 68.04, 47.86, 30.65, 29.47, 24.39, 22.96, 14.94, 12.29. MS [m/z (%)]: 294.18 (17.3). Anal. Calcd for $C_{17}H_{26}O_4$: C, 69.36; H, 8.90. Found: C, 69.50; H, 9.06.

2-Hydroxycyclohexyl 2-benzamidoacetate (entry **16**).

Column chromatography purification on silica gel elution with EtOAc gave a white foam (0.25 g, 91%); R_f 0.62 (EtOAc). IR (liquid film): 3500-3170 (br), 3050, 2948, 1735, 1695, 1250 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ_{ppm} = 7.81-7.78 (m, 2 H, aryl), 7.68 (s, 1 H, NH, exchangeable with D_2O), 7.46-7.34 (m, 3 H, aryl), 4.69-4.68 (m, 1 H, CO_2CH), 4.15 (complex, 3 H, NCH_2, *H*COH), 3.49 (s, 1 H, OH, exchangeable with D_2O), 1.95 (br s, 2 H, CH_2), 1.65 (br s, 2 H, CH_2), 1.23 (br, 4 H, 2 CH_2). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ_{ppm}: 170.16, 168.21, 133.44, 131.77, 128.49, 127.21, 79.27, 72.32, 42.24, 32.77, 29.98, 23.86, 23.76. MS [m/z (%)]: 277.13 (9.4). Anal. Calcd for $C_{15}H_{19}NO_4$: C, 64.97; H, 6.91; N, 5.05. Found: C, 64.85; H, 6.97; N, 5.19.

2-Hydroxy-2-methylpropyl 2-benzamidoacetate (entry **17**).

Column chromatography purification on silica gel elution with *n*-hexane-EtOAc (1:1) gave a bright brown foam (0.24 g, 94%); R_f 0.2 (50 % *n*-hexane-EtOAc). IR (liquid film): 3450-3190 (br), 3046, 2965, 1732, 1691, 1254 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ_{ppm} = 7.85 (s, 1 H, NH, exchangeable with D_2O), 7.75-7.73 (m, 2 H, aryl), 7.39-7.24 (m, 3 H, aryl), 4.09 (d, *J* = 5.1 Hz, 2 H, NCH_2), 3.92 (s, 2 H, CO_2CH_2), 3.67 (s, 1 H, OH, exchangeable with D_2O), 1.11 (s, 6 H, 2 CH_3). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ_{ppm}: 170.13, 168.42, 133.32, 131.79, 128.46, 127.25, 72.50, 69.45, 41.94, 25.91. MS [m/z (%)]: 251.12 (14.9). Anal. Calcd for $C_{13}H_{17}NO_4$: C, 62.14; H, 6.82; N, 5.57. Found: C, 62.23; H, 6.97; N, 5.76.

Supplementary Material ((optional))

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/MS-number.

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Author Contribution Statement

S. Behrouz and *M. N. Soltani Rad* have designed the project and experiments, synthesized the catalyst, carried out the spectroscopic data analyses and wrote the manuscript. *M. A.* Piltan achieved the synthesis of all compounds using the catalyst. *M.M. Doroodmand* performed catalyst characterization and data analyses.

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