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Sulfamic acid grafted to cross-linked chitosan by dendritic units: a bio-based, highly efficient and heterogeneous organocatalyst for green synthesis of 2,3-dihydroquinazoline derivatives†

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In this work, novel cross-linked chitosan by the G1 dendrimer from condensation of melamine and toluene-2,4-diisocyante terminated by sulfamic acid groups (CS-TDI-Me-TDI-$NHSO_3H$), as a bio-based and heterogeneous acidic organocatalyst, was designed and prepared. Also, the structure of the prepared organocatalyst was characterized by Fourier transform infrared spectroscopy (FT-IR), field emission scanning electron microscopy (FESEM), energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD) and thermogravimetric analysis/derivative thermogravimetry (TGA/DTA). Subsequently, the catalytic performance of the biobased and dendritic CS-TDI-Me-TDI-$NHSO_3H$, as a multifunctional solid acid, was evaluated for the preparation of 2,3-dihydroquinazoline derivatives through a three-component reaction by following green chemistry principles. Some of the advantages of this new protocol include high to excellent yields and short reaction times as well as easy preparation and remarkable catalyst stability of the introduced acidic organocatalyst. The CS-TDI-Me-TDI-SO_3H catalyst can be used for up to five cycles for the preparation of quinazoline derivatives with a slight decrease in its catalytic activity.

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Introduction

Polysaccharide-based scaffolds have been widely used in different fields such as drug delivery, vaccines, wound dressing materials, cosmetics, food additives and packaging, environmental applications including water treatment, and heterogeneous organocatalysts due to their bioactivity, biodegradability and biocompatibility in recent decades.[1–14] Hence, the use of renewable biopolymers such as cellulose, chitin, sodium alginate, and especially chitosan for the design and preparation of efficient biodegradable and heterogeneous organocatalytic systems would be very desirable.[11,15–39] Among these scaffolds, chitosan (CS) is one of the most unique and widely used biopolymers, a natural and active cationic amino polysaccharide obtained from the alkaline *N*-deacetylation of chitin.[8,24,40–47] Indeed, chitosan has numerous applications in various fields such as preparation of new bio-based materials,[48–52] heterogeneous catalytic systems,[38,53–55] water purification, metal extraction,[56–59] electrolyte-based fuel cells,[60–62] sensors,[6,63] corrosion protection,[64] *etc.* However, many research attempts are being made to provide functional chitosan derivatives with chemical modifications. Some of the advantages of using chitosan in various applications include low cost, chemical stability, desirable hydrophilicity, having proper functional groups for chelation of metals, non-toxicity, and environmental friendliness. Compared to homogeneous catalytic systems, heterogeneous ones are much more efficient for multiple and continous use in the chemical synthesis.[65–67] Indeed, heterogeneous catalyst systems benefit from easy removal, recovery and recycling of the catalyst compared to homogeneous catalysts.[68] Therefore, chitosan application as a new support material for heterogeneous catalysis is increasing.[69,70] Also, the use of ligands containing multi-amine groups in a chain or dendrimer increases the catalytic efficiency by increasing the number of active sites.

Melamine-based dendrimer amines (MDAs) are ideal dendrimer ligands, first reported in 2000 by Simanek and Zhang. MDAs have received a great deal of attention due to the strong binding of amine sites and increasing of the surface hydrophilicity.[71–75] On the other hand, sulfamic acid (H_2NSO_3H) is a common sulfur-containing amino acid with mild acidity, which has been used to replace conventional Lewis and Brønsted acid catalysts.[76–78] Noteworthy, sulfamic acid also exists as $H_3N^+SO_3^-$ zwitterionic units insoluble in non-polar organic solvents. Hence, its catalytic properties arise from its zwitterionic nature and shows excellent activity in acid-catalyzed organic transformations. Thus, it has been widely

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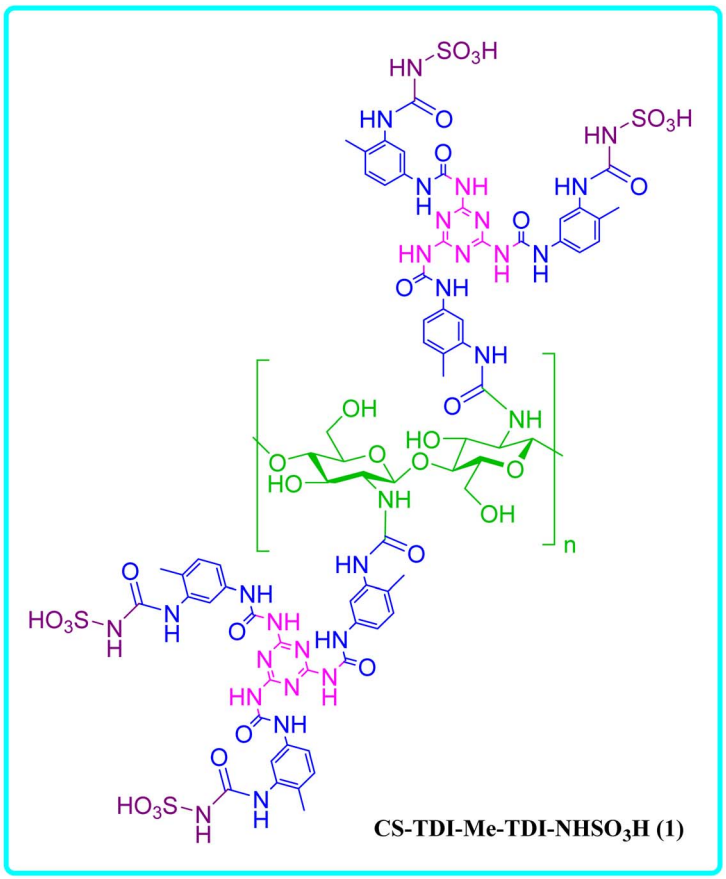
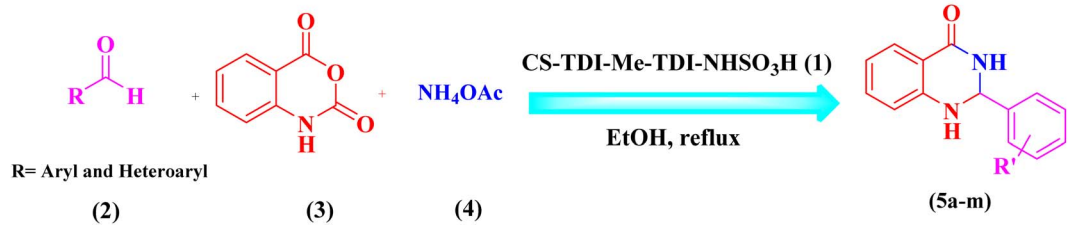




Scheme 1 CS-TDI-Me-TDI-NHSO$_3$H (**1**), as solid acid catalyst, for green synthesis of 2,3-dihydroquinazoline derivatives by using aldehyde derivatives (**2**), isatoic anhydride (**3**) and ammonium acetate (**4**) in EtOH under reflux conditions.

used, as an acidic catalyst, in reactions such as Michael addition reaction,[71] Pechmann reaction,[79] Beckmann rearrangement reaction,[80] imino Diels–Alder reaction,[81] and functional group protection[82] and deprotection[83] reactions.

2,3-Dihydroquinazolines are a group of heterocyclic compounds that have a pyrimidine nucleus in their structure.[84–88] Also, they have received increased attention due to their wide range of biological properties such as anesthetic,[89] anti-cancer,[90] muscle relaxant[91] and sedative properties.[92] Therefore, synthesis of 2,3-dihydroquinazoline derivatives has attracted the attention of organic and pharmaceutical chemists, leading to various methods for the preparation of 2,3-dihydroquinazoline derivatives in order to achieve higher reaction efficiency.[70,93–105] Most of these reported methods have disadvantages such as multi-stage preparation methods, long reaction time, low efficiency, hard reaction conditions, and the use of precious metals or toxic reagents. Thus, using new methods for the synthesis of 2,3-dihydroquinazolines under desired reaction conditions is important.

In the present work, sulfamic acid grafted to cross-linked chitosan by dendritic units (CS-TDI-Me-TDI-NHSO$_3$H, **1**) organocatalyst was designed, prepared and characterized. The CS-TDI-Me-TDI-NHSO$_3$H was used as a heterogeneous and green nanocatalyst for the synthesis of 2,3-dihydroquinazoline derivatives (Scheme 1).

Results and discussion

The prepared CS-TDI-Me-TDI-HNSO$_3$H organocatalyst (**1**) was characterized using various suitable techniques including FT-IR, FESEM, XRD, TGA and EDS.

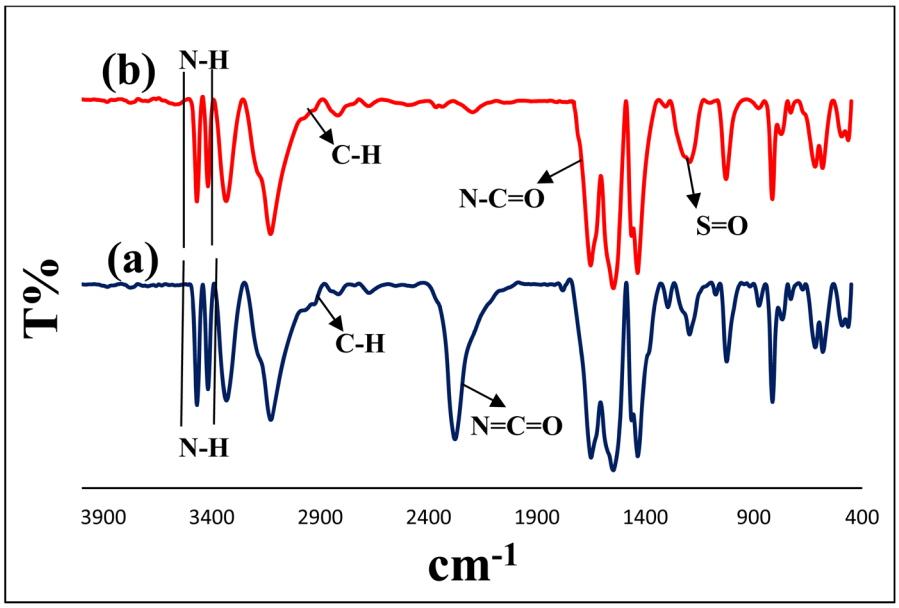


Fig. 1 FTIR spectra of melamine–toluene 2,4-diisocyanate intermediate (**I**, a) and CS-TDI-Me-TDI-$HNSO_3H$ bio-based material (**1**, b).

Fig. 1 shows the FT-IR spectra of melamine–toluene 2,4-diisocyanate intermediate (**I**, a) and CS-TDI-Me-TDI-$HNSO_3H$ (**1**, b). According to Fig. 1a, the absorption bands at 3468–3334 cm^{-1} are attributed to the stretching vibration of N–H bonds of amin groups. Also, absorption band at 2926 cm^{-1} belongs to the stretching vibration of C–H aliphatic bonds. In addition, the adsorption bands at 2276 cm^{-1} and 1652 cm^{-1} correspond to the vibration of N=C=O and C=O bonds of the amide. As shown in Fig. 1b, the absorption bands at 3470–3336 cm^{-1} are attributed to the stretching vibration of N–H bonds of the amine groups. Also, the absorption band at 2976 cm^{-1} belongs to the stretching vibration of C–H aliphatic bonds. Whereas, the adsorption band at 1654 cm^{-1} is related to the stretching vibration of C=O bond of amide groups. Also, the characteristic bands at 1208 cm^{-1} and 1026 cm^{-1} correspond to the asymmetric and symmetric S=O stretching vibration in the SO_3H group, respectively.

Fig. 2 shows the XRD pattern of CS-TDI-Me-TDI-$HNSO_3H$ (**1**). There are symmetrical reflections at 2θ of 17.56°, 21.52°, 26.08°, 28.71°, and 29.72° which are characteristic of the CS-TDI-Me-TDI-$HNSO_3H$ (**1**) structure according to the standard XRD

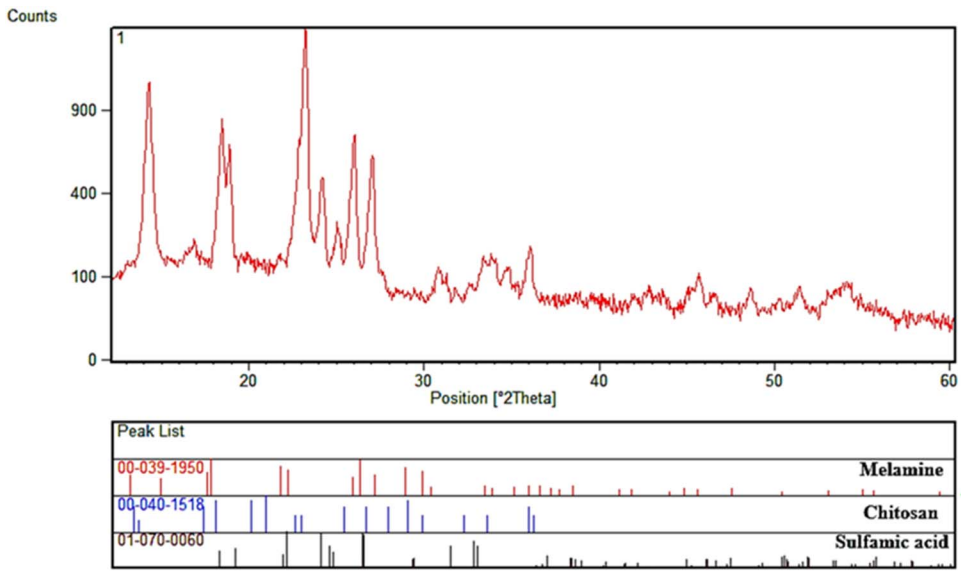


Fig. 2 Wide-angle XRD pattern of CS-TDI-Me-TDI-$HNSO_3H$ nanomaterial (**1**).

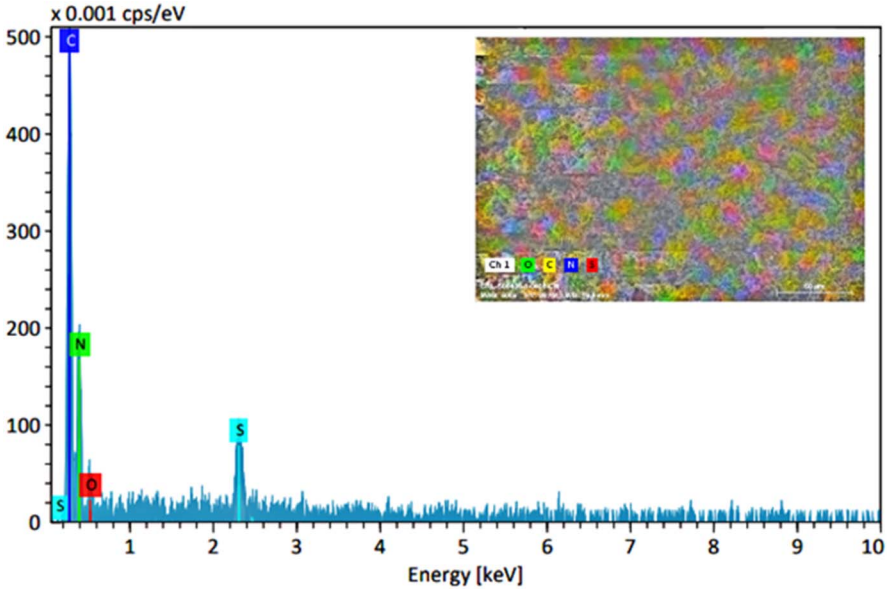


Fig. 3 EDS spectra of the CS-TDI-Me-TDI-$HNSO_3H$ organocatalyst (**1**).

patterns of melamine (JCPDS card no. 00-039-1950), chitosan (JCPDS card no. 00-040-1518), and H_2NSO_3H (JCPDS card no. 01-070-0060). As can be seen, the results obtained from the XRD pattern of CS-TDI-Me-TDI-$HNSO_3H$ (**1**) confirm the successful preparation of the desired nanomaterial.

Fig. 3 shows the EDS analysis related to the CS-TDI-Me-TDI-$HNSO_3H$ organocatlyst (**1**), which confirms the presence of C, O, N, and S elements in its structure. Therefore, the presence of S element indicates the grafting of H_2NSO_3H on the chitosan backbone. Also, EDS mapping analysis shows uniform particle distribution of the structure.

FESEM images of CS-TDI-Me-TDI-$HNSO_3H$ (**1**) nanomaterial (**1**) are shown in Fig. 4. FESEM images of structure of CS-TDI-Me-TDI-$HNSO_3H$ shows that the morphology of chitosan has changed from sheets to irregular particles, which confirms the formation of the desired structure. Also, these particles have a uniform dispersion and average particle size of 25–44 nm.

Using thermogravimetric analysis (TGA), the thermal stability of the prepared catalyst (**1**) was investigated in the temperature range of 50–500 °C. As shown in Fig. 5, two weight loss steps were observed between 270 and 400 °C, Since the pristine chitosan is degraded at 200–220°,[106] this degradation at the temperature range of 270–400 °C indicates that the organic units on the surface of chitosan have been linked by toluene diisocyanate, which affects the thermal stability of chitosan and degradation takes place at a higher temperature.

Optimization of conditions for the synthesis of 2,3-dihydroquinazoline derivatives in the presence of CS-TDI-Me-TDI-$HNSO_3H$ organocatalyst (1)

In this section, the efficacy of CS-TDI-Me-TDI-$HNSO_3H$ nanomaterial (**1**) in the model reaction for the synthesis of 2, 3-dihydroquinazoline derivatives was investigated. Therefore, different parameters including solvent, catalyst loading, temperature, and reaction time were investigated to determine the optimal reaction conditions (Table 1). The model reaction was investigated in the presence of 4-chloroaldehyde (**2a**, 0.5 mmol), isatoic anhydride (**3**, 0.5 mmol) and ammonium acetate (**4**, 1.5 mmol) for the synthesis of 2,3-dihydroquinazoline derivatives in various conditions. First, the model reaction was run without catalyst using various solvents at different temperatures (Table 1, entries 1–4). As shown in Table 1, without catalyst, the model reaction did not proceed to afford the desired product after 1 h. However, in the presence of 15 mg of CS-TDI-Me-TDI-$HNSO_3H$ organocatalyst (**1**), the desired product **5a** was prepared in medium to excellent yields (57 to 97%, Table 1, entries 5–8). The progress of the model reaction to afford the desired product **5a** in EtOH was investigated at temperatures rather than reflux conditions (Table 1, entries 9 and 10). Based on the obtained results, EtOH under reflux conditions can be considered as the desirable solvent. Afterward, to determine the desirable amount of catalyst, the model reaction was carried out in EtOH under reflux conditions in the presence of 10, 15 and 20 mg of CS-TDI-Me-TDI-$HNSO_3H$ organocatalyst (**1**) (Table 1, entries 10–12). Consequently, 15 mg of CS-TDI-Me-TDI-$HNSO_3H$ organocatalyst (**1**) loading in EtOH under reflux conditions were selected as the optimal reaction conditions.

After that, in order to extend the catalytic application of CS-TDI-Me-TDI-$HNSO_3H$ (**1**), three-component condensation of aldehyde derivatives (**2a–m**, 0.5 mmol), isatoic anhydride (**3**, 0.5 mmol), and ammonium acetate (**4**, 1.5 mmol) was performed under optimal conditions for the synthesis of 2,3-dihydroquinazoline derivatives (**5a–m**). The results are summarized in Table 2.

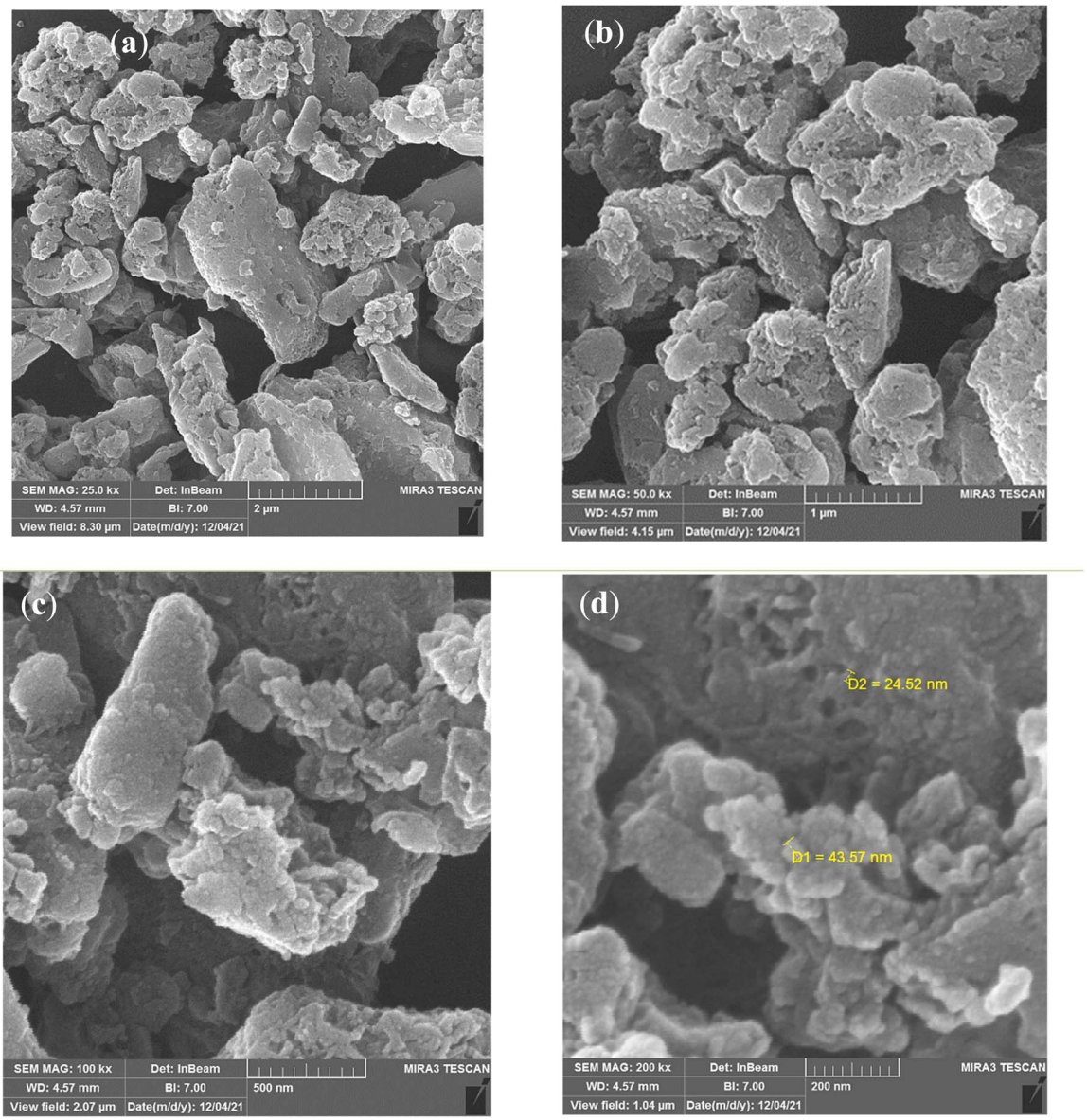
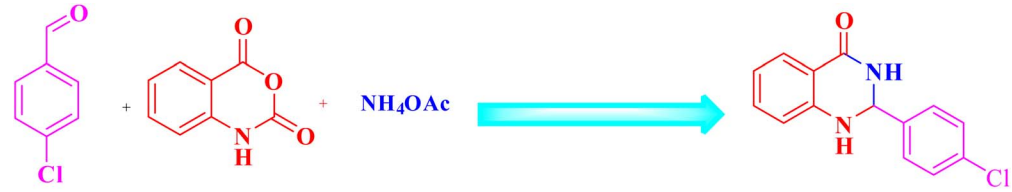


Fig. 4 FESEM images of CS-TDI-Me-TDI-$HNSO_3H$ nanomaterial (**1**).

Fig. 5 TGA curves of CS-TDI-Me-TDI-$HNSO_3H$ organocatalyst (**1**).

Table 1 Screening of optimized conditions for three component reaction of 4-chloroaldehyde (**2a**), isatoic anhydride (**3**) and ammonium acetate (**4**) to afford 2,3-dihydroquinazoline derivative **5a** in the presence of CS-TDI-Me-TDI-$HNSO_3H$ solid acid (**1**)[a]

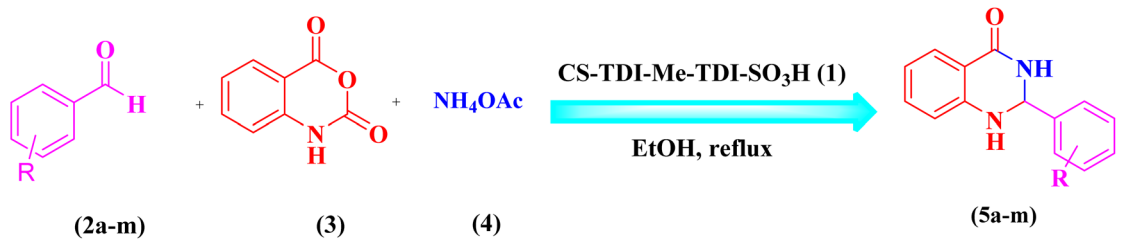


(2a) (3) (4) (5a)

Entry	Catalyst	Conditions	Catalyst loading (mg)	Time (min)	Yield (%)
1	—	EtOH/RT	—	60	Trace
2	—	CH_2Cl_2/RT	—	60	—
3	—	H_2O/RT	—	60	—
4	—	DMF/RT	—	60	Trace
5	**CS-TDI-Me-TDI-$HNSO_3H$ (1)**	**EtOH/reflux**	**15**	**15**	**97**
6	CS-TDI-Me-TDI-$HNSO_3H$ (**1**)	H_2O/reflux	15	60	57
7	CS-TDI-Me-TDI-$HNSO_3H$ (**1**)	CH_2Cl_2/reflux	15	60	40
8	CS-TDI-Me-TDI-$HNSO_3H$ (**1**)	DMF/reflux	15	60	62
9	CS-TDI-Me-TDI-$HNSO_3H$ (**1**)	EtOH/RT	15	40	50
10	CS-TDI-Me-TDI-$HNSO_3H$ (**1**)	EtOH/50 °C	15	20	87
11	CS-TDI-Me-TDI-$HNSO_3H$ (**1**)	EtOH/reflux	10	15	80
12	CS-TDI-Me-TDI-$HNSO_3H$ (**1**)	EtOH/reflux	20	45	83

[a] Reaction conditions: 4-chloroaldehyde (**2a**, 0.5 mmol), isatoic anhydride (**3**, 0.5 mmol) and ammonium acetate (**4**, 1.5 mmol) in the presence of CS-TDI-Me-TDI-$HNSO_3H$ (**1**) unless otherwise noted.

Table 2 Synthesis of 2,3-dihydroquinazoline derivatives (**5a–m**) through the three-component condensation of aldehyde derivatives (**2a–m**), isatoic anhydride (**3**), and ammonium acetate (**4**) in the presence of CS-TDI-Me-TDI-$HNSO_3H$ organocatalyst (**1**)[a]



(2a-m) (3) (4) (5a-m)

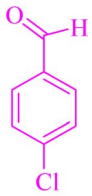
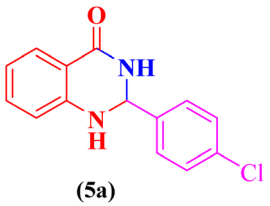
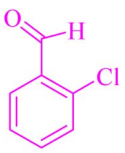
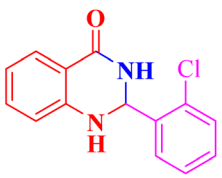
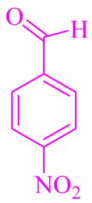
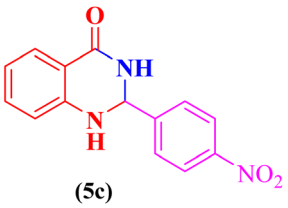
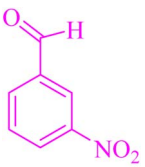
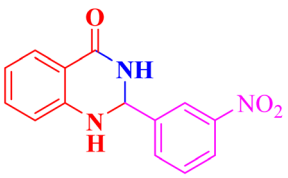
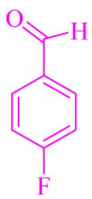
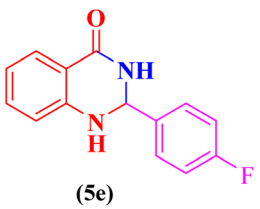
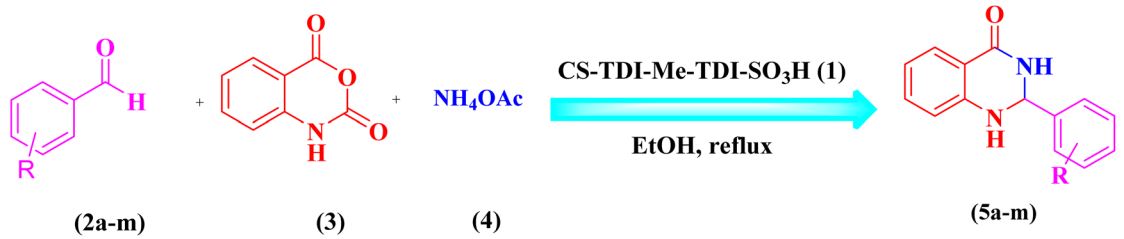
Entry	Aldehyde	Product	Time (min)	Yield (%)	M.p. (°C) (Obs.)	M.p. (°C) (Lit.)
1	 (2a)	 (5a)	15	97	204–206	203–206 (ref. 107)
2	 (2b)	 (5b)	15	95	207–209	206–208 (ref. 108)
3	 (2c)	 (5c)	25	87	198–201	200–202 (ref. 107)
4	 (3d)	 (5d)	55	80	190–192	190–193 (ref. 107)
5	 (2e)	 (5e)	25	87	194–195	193–197 (ref. 109)

Table 2 (*Contd.*)



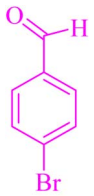
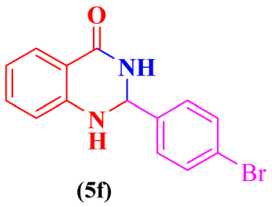
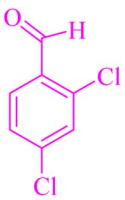
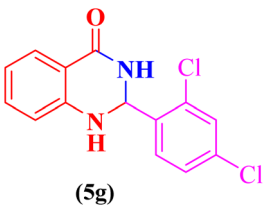
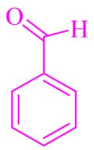
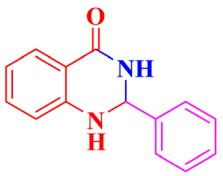
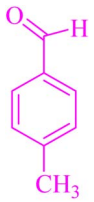
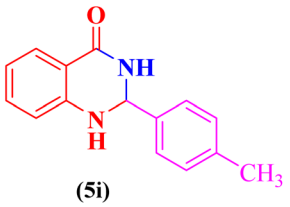
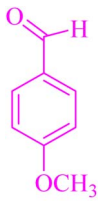
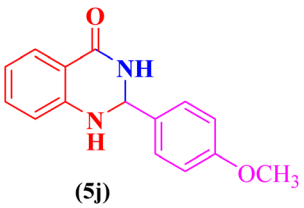
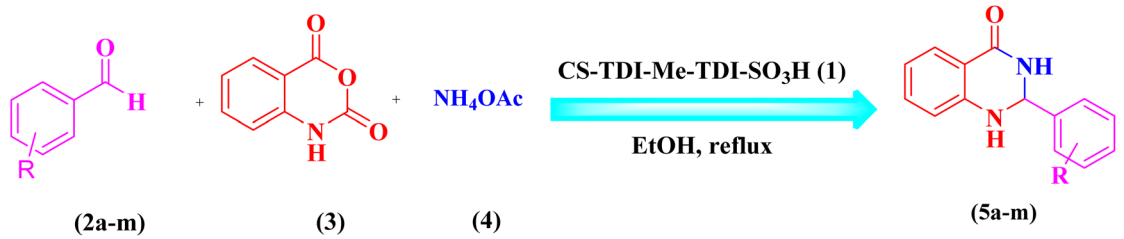
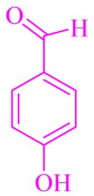
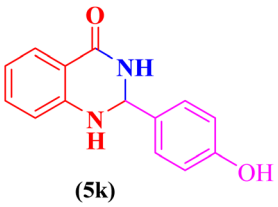
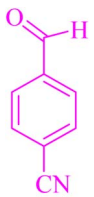
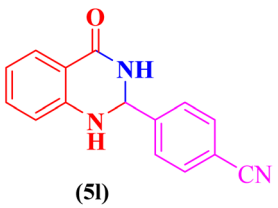
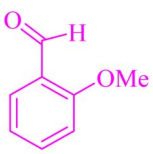
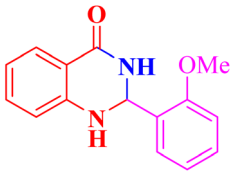
Entry	Aldehyde	Product	Time (min)	Yield (%)	M.p. (°C) (Obs.)	M.p. (°C) (Lit.)
6	 (2f)	 (5f)	25	86	197–199	196–198 (ref. 109)
7	 (2g)	 (5g)	15	90	165–169	166–169 (ref. 107)
8	 (2h)	 (5h)	20	90	209–211	208–210 (ref. 109)
9	 (2i)	 (5i)	30	89	199–202	198–201 (ref. 110)
10	 (2j)	 (5j)	45	90	179–181	178–182 (ref. 87)

Table 2 (*Contd.*)



Entry	Aldehyde	Product	Time (min)	Yield (%)	M.p. (°C) (Obs.)	M.p. (°C) (Lit.)
11	 (2k)	 (5k)	25	86	214–217	213–215 (ref. 109)
12	 (2l)	 (5l)	35	92	350–352	351–352 (ref. 87)
13	 (2m)	 (5m)	40	91	166–168	165–167 (ref. 111)

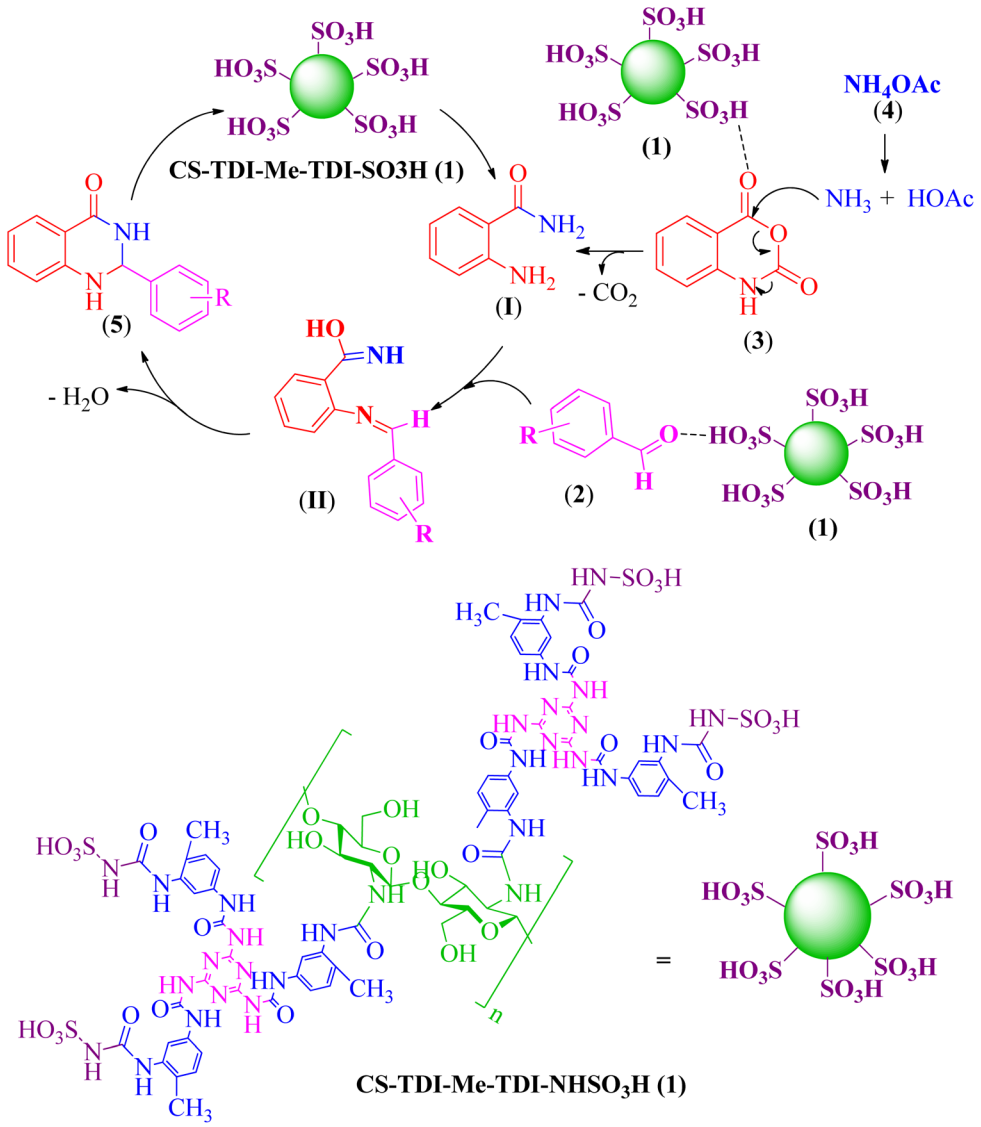
[a] Reaction conditions: aldehyde derivatives (**2a–m**, 0.5 mmol), isatoic anhydride (**3**, 0.5 mmol) and ammonium acetate (**4**, 1.5 mmol) in the presence of CS-TDI-Me-TDI-$HNSO_3H$ (**1**, 15 mg) in EtOH under reflux conditions.

The possible mechanism for the synthesis of 2,3-dihydroquinazoline derivatives in the presence of CS-TDI-Me-TDI-$HNSO_3H$ (1)

Scheme 2 shows the proposed mechanism for the synthesis of 2,3-dihydroquinazoline derivatives. CS-TDI-Me-TDI-$HNSO_3H$ organocatalyst (**1**) has Brønsted acidic centers. Hence, it activates carbonyl groups in isotonic anhydride by forming a hydrogen bond to facilitate the nucleophilic addition of ammonium acetate (**4**) and forming the intermediate **I**. Next, this intermediate reacts with aldehyde derivatives and forms intermediate **II**. Finally, by removing H_2O from intermediate **II**, 2,3-dihydroquinazoline derivatives **5** are synthesized as the desired product.

Also, the reusability of CS-TDI-Me-TDI-$HNSO_3H$ solid acid catalyst (**1**) was studied in the synthesis of 2,3-dihydroquinazoline derivative **5a**. For this purpose, the CS-TDI-Me-TDI-$HNSO_3H$ (**1**) was separated by filtration, washed with water and acetone, and then dried at 70 °C for 24 h. The recycled organocatalyst in each run was used after activation for the preparation of 2,3-dihydroquinazoline derivative **5a** in the next run. This reaction was repeated up to five times and no significant reduction was observed in the CS-TDI-Me-TDI-$HNSO_3H$ organocatalyst (**1**) efficiency (Fig. 6).

Table 3 compares the efficiency of dendritic CS-TDI-Me-TDI-$HNSO_3H$ organocatalyst (**1**) with other catalysts for the synthesis of desired 2,3-dihydroquinazoline derivative **5a**. For this comparison, several parameters, *e.g.*, the reaction time,



Scheme 2 The proposed mechanism for the synthesis of 2,3-dihydroquinazoline derivatives **5** catalyzed by the biobased multifunctional CS-TDI-Me-TDI-$HNSO_3H$ solid acid (**1**).

temperature, and the reaction yield, were taken into consideration. It can be seen that CS-TDI-Me-TDI-$HNSO_3H$ heterogeneous catalyst (**1**) showed higher efficiency than previously reported catalysts for the synthesis of 2,3-dihydroquinazoline derivatives.

Experimental

Materials and methods

The CS-TDI-Me-TDI-$HNSO_3H$ nanomaterial (**1**) was purely prepared by modifing of known methods for similar materials having the same functional groups. Chitosan (CS, MW = 100 000–300 000 Da) was obtained from Acros Organics. Melamine (Me) and triethylamine (TEA) were provided by Sigma-Aldrich. Tetrahydrofuran (THF), sulfamic acid (H_2NSO_3H), and toluene-2,4-diisocyanate (TDI) were purchased from Merck-Millipore. Other chemical compounds were supplied by Merck and Aldrich Chemical Co. Characterization of the heterogeneous CS-TDI-Me-TDI-H_2NSO_3H (**1**) organocatalyst was performed using FESEM (TESCAN-MIRA III), EDS (TESCAN-MIRA II), TGA (STA 504, Bahr Co.), and XRD (Bourevestnik DRON-8) analyses. ^1H NMR (500 MHz) spectra recorded on a Bruker DRX-500 Avance spectrometers in DMSO, as the solvent, at ambient temperature. FT-IR spectra were recorded as KBr pellets on a Shimadzu FT-IR-8400S spectrometer. Analytical thin-layer chromatography (TLC) was performed using Merck 0.2 mm silica gel 60F-254 Al-plates for reaction monitoring. Melting points were determined using an Electrothermal 9100 apparatus.

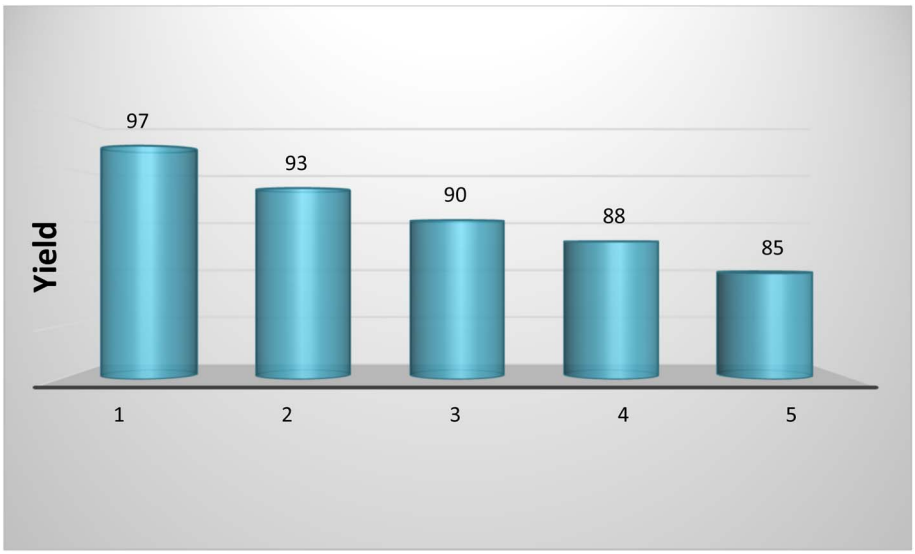


Fig. 6 Reusability of the CS-TDI-Me-TDI-$HNSO_3H$ organocatalyst (**1**) in the model reaction to afford **5a**.

Table 3 Comparison of the catalytic efficiency of CS-TDI-Me-TDI-$HNSO_3H$ (**1**) with other heterogeneous catalysts for 4-cholorobenzaldhyde

Entry	Catalyst	Time (min)	Solvent/temperature conditions	Yield (%)	Reference
1	CS-TDI-Me-TDI-$HNSO_3H$ (**1**)	15	EtOH/reflux	97	This work
2	Wang-OSO_3H	40	H_2O/100 °C	84	108
3	Titanium silicon oxide nanopowder	120	H_2O/100 °C	94	112
4	Montmorillonite-KSF	150	Solvent-free/100 °C	93	113
5	$Al(H_2PO_4)_3$	540	Solvent-free/100 °C	70	114
6	Co-aminobenzamid@Al-SBA-15	24	EtOH/reflux	96	115

General method for preparation of CS-TDI-Me-TDI-$HNSO_3H$ organocatalyst (1). To a round button flask, a mixture of melamine (4 mmol, 0.5 g), TDI (12 mmol, 2 mL) and THF (15 mL) was added and stirred at room temperature under nitrogen atmosphere for 24 h. The obtained white solid (**I**) was filtered off and washed with THF, then dried in a vacuum oven at 60 °C for 12 h (Scheme 3). Also, $H_3N^+SO_3^-$ (8 mmol, 0.776 g) and TEA (10 mmol, 1.4 mL) were added to THF (5 mL) and stirred for 2 h. Subsequently, the white solid (**I**) was added to the mixture and stirred for another 24 h at room temperature. Then, CS (0.5 g) was added and refluxed for 24 h under nitrogen atmosphere. Finally, the obtained white powder was filtered and washed with THF and EtOH and dried at 60 °C for 24 h (Scheme 3).

General procedure for the synthesis of 2,3-dihydroquinazoline derivatives. A mixture of aldehyde derivatives (**2**, 0.5 mmol), isatoic anhydride (**3**, 0.5 mmol), ammonium acetate (**4**, 1.5 mmol), CS-TDI-Me-TDI- $HNSO_3H$ (**1**, 15 mg), and EtOH (5 mL) was stirred at 80 °C. After completion of the reaction, the organocatalyst was filtered and washed with acetone. The products were purified by recrystallization from EtOH. The products were identified by melting point measurement, FT-IR and ^{1}HNMR spectroscopy.

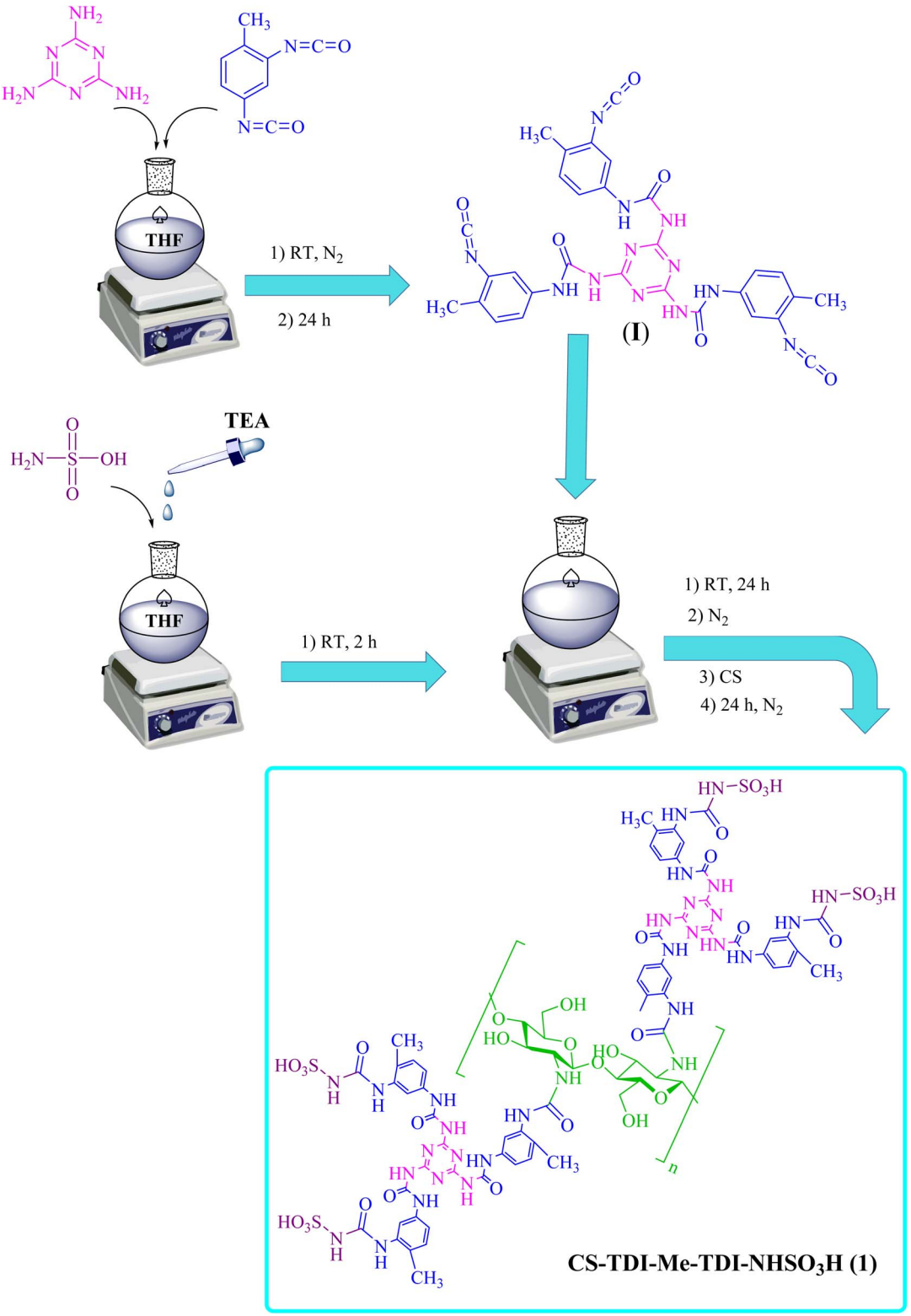
Selected spectral data

2-(4-Chlorophenyl)-2,3-dihydroquinazolin-4(1H)-one ***(2a).*** Melting point: 212–214 °C; FTIR (KBr, cm^{-1}): 3305, 3184, 3062, 1654, 1606, 1431, 1090, 749 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ_H (ppm) = 5.77 (s, 1H, CH), 6.68 (t, 1H, Ar–H), 6.74 (d, 1H, Ar–H), 7.10 (s, 1H, NH), 7.24 (t, 1H, Ar–H), 7.45 (d, 1H, Ar–H), 7.50 (d, 1H, Ar–H), 7.61 (d, 1H, Ar–H), 8.27 (s, 1H, CONH).

2-(2-Chlorophenyl)-2,3-dihydroquinazolin-4(1H)-one ***(5b).*** Melting point: 207–209 °C; FTIR (cm^{-1}): 3310, 3207, 3050, 1660, 1492, 1479; ^{1}H NMR (500 MHz, DMSO-d_6): δ_H (ppm) 6.14 (s, 1H), 6.72 (t, 1H, J = 7.5 Hz), 6.77 (d, 1H, J = 8.1 Hz), 7.01 (s, 1H), 7.26 (t, 1H, J = 7.7 Hz), 7.40 (d, 2H, J = 4.1 Hz), 7.49 (d, 1H, J = 4.1 Hz), 7.66 (d, 2H, J = 6.7, Hz), 8.21 (s, 1H).

2-(4-Methylphenyl)-2,3-dihydroquinazolin-4(1H)-one ***(5i).*** Melting point: 199–202 °C; FTIR (cm^{-1}): 3300, 3170, 3032, 2931, 2827, 1510, 1249; ^{1}H NMR (500 MHz, DMSO-d_6): δ_H (ppm) 2.29 (s, 3H), 5.70 (s, 1H), 6.66 (t, 1H, J = 7.4 Hz), 6.73 (d, 1H, J = 8.1 Hz), 7.04 (s, 1H), 7.19 (d, J = 7.6 Hz, 1H), 7.23 (t, J = 8.1 Hz, 1H), 7.37 (d, J = 7.8 Hz, 2H), 7.61 (d, J = 7.6 Hz, 1H), 8.22 (s, 1H); δ_C (ppm) ^{13}C NMR (125 MHz, DMSO-d_6): 162.70, 152.90, 141.98, 134.99, 130.28, 129.65, 128.21, 127.64, 127.58, 126.88, 126.30, 121.23, 21.23.

2-(4-Methoxylphenyl)-2,3-dihydroquinazolin-4(1H)-one ***(5j).*** Melting point: 179–181 °C; FTIR (cm^{-1}): 3301, 3170, 3029, 2930, 2825, 1511, 1248; ^{1}H NMR (500 MHz, DMSO-d_6): δ_H (ppm) 3.74 (s, 3H), 5.70 (s, 1H), 6.67 (t, 1H, J = 7.6 Hz), 6.74 (d, 1H, J = 8.1 Hz),



Scheme 3 Schematic representation of CS-TDI-Me-TDI-$HNSO_3H$ (1) preparation steps.

6.95 (d, 2H, $J = 8.4$), 7.00 (s, 1H), 7.23 (t, $J = 8.0$ Hz, 1H), 7.42 (d, $J = 7.6$ Hz, 2H), 7.61 (d, $J = 7.6$ Hz, 1H), 8.17 (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ_C (ppm) 162.62, 152.84, 135.49, 135.14, 130.07, 126.94, 126.79, 126.37, 124.56, 120.92, 118.30, 114.36, 55.74.

Conclusions

In this paper, a new heterogeneous acidic catalyst based on the renewable and biodegradable chitosan polymer, *i.e.*, CS-TDI-

Me-TDI-$HNSO_3H$, was prepared and characterized using various spectral and analytical techniques. Subsequently, CS-TDI-Me-TDI-$HNSO_3H$ was used, as a solid acid, for the synthesis of 2,3-dihydroquinazoline derivatives under green conditions. The desired 2,3-dihydroquinazoline derivatives were prepared in high to excellent yields under optimal conditions. Low catalyst loading, mild reaction conditions and very short reaction times as well as reusability of the catalyst for at least four consecutive catalytic cycles without significant loss of its activity are the advantages of this new protocol.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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