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Synthesis of a novel acidic ionic liquid catalyst and its application for preparation of pyridines via a cooperative vinylogous anomeric-based oxidation

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Abstract

In the current study, a novel acidic ionic liquid catalyst based on 8-hydroxyquinoline, namely 8,8′,8″-([1,3,5-triazine-2,4,6-triyl]tris[oxy])tris(1-sulfoquinolin-1-ium) chloride (TTS), was designed and synthesized. The structure of the prepared acidic ionic liquid (AIL) was fully investigated by using Fourier transform infrared (FT-IR) spectroscopy, energy dispersive X-ray (EDX) analysis, thermogravimetric analysis/differential thermal analysis (TGA/DTA), ^{1}HNMR, ^{13}CNMR and mass spectroscopy. Then, the catalytic performance of described AIL was successfully inspected toward the four-component synthesis of pyridine derivatives via a cooperative vinylogous anomeric-based oxidation.

Supplementary Information The online version of this article (https://doi.org/10.1007/s11164-020-04361-y) contains supplementary material, which is available to authorized users.

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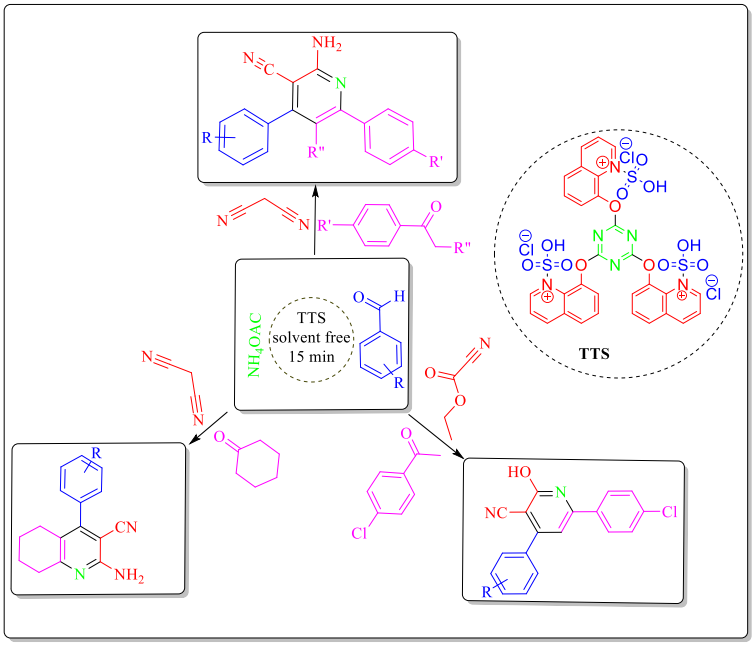
Graphic abstract

Novel AIL (TTS) showed a very high efficiency in the synthesis of pyridines.



Keywords Acidic ionic liquid · Anomeric-based oxidation · Cooperative vinylogous anomeric-based oxidation · Ionic liquid · Pyridine

Introduction

Ionic liquids (ILs) are composed entirely of ions, and their high steric hindrances cause the ions to bond poorly to each other, resulting in their melting point below 100 °C or even at room temperature [1]. These compounds have distinctive properties that in addition to low melting point, include high polarity, extremely low vapor pressure, low flammability, high temperature range in the liquid state, easy recyclability, adjustable mixability with water and other solvents, conductivity and thermal, chemical and electrochemical stability [2]. In addition, the physicochemical properties of these compounds can be adjusted by changing the cation structure and the cation–anion combination [3]. Due to the mentioned properties, in recent years, much attention has been paid to these compounds and have found many applications in various fields such as pharmacy [4], nanomaterials [5], and catalytic chemistry [6, 7]. Based on the properties, ILs can be classified into three categories: acidic, alkaline and neutral. An AIL can be defined as a low melting ionic salt with acidic characteristics [8]. The use of AILs in biomass processes has received a great deal of

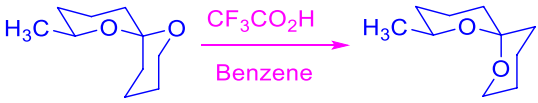
attention in the last ten years [9, 10]. AILs have been used extensively as catalysts in esterification [11], alkylation [12–16], acetylation [17], heterocyclic synthesis reactions [18], dehydration [19], oxidation [20] and polymerization [21] reactions.

The design and application of high-efficiency catalysts in the synthesis of organic materials has attracted much attention [22]. Organocatalysts had special superiority in the production of pharmaceutical materials compared to (transition) metal catalysts. In addition, organocatalysts are not usually expensive, are stable, are easy to get accessible, have low toxicity and are not sensitive to moisture and oxygen [23–35]. Despite their controversy as greener compounds, ILs can be considered as organocatalysts [36].

The preference of the axial position for an electron acceptor group (electronegative atom) adjacent to an electron donor group (lone pairs) over the equatorial position is an important stereoelectronic phenomenon called the anomeric effect [37–45] (Scheme 1).

Scientists have proposed hypotheses for the superiority of the axial position [46]. Figure 1 shows the most frequently considered explanations for these hypotheses in the case of tetrahydropyrans. According to Edward, the reason for the superiority of the axial position over the equatorial position is the less repulsion between polar interactions in the axial position than the equatorial position (Fig. 1a) [47]. Of course, according to Lemiux and Chou, electrostatic dipolar interactions can be considered as coulombic interactions if the bond moments responsible for Edward's

Scheme 1 Axial preference for acceptor group at the anomeric position



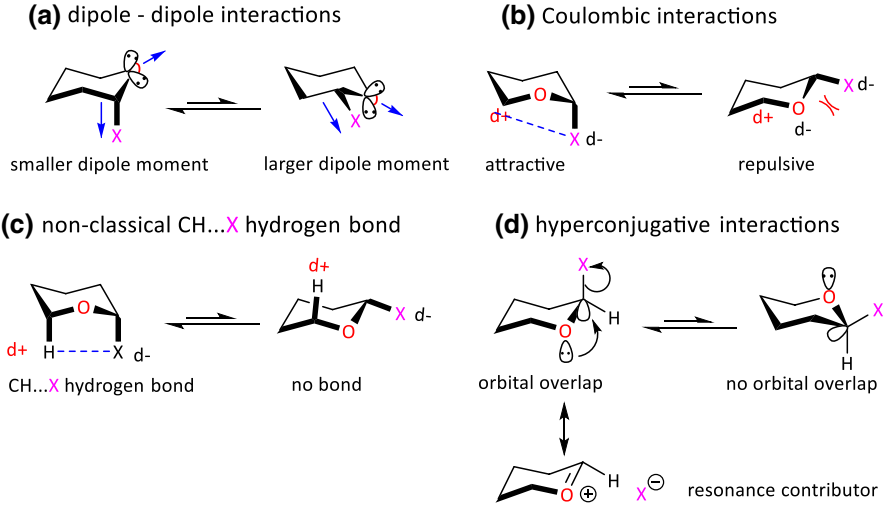


Fig. 1 Most frequently considered explanations hypotheses have been proposed to account for the anomeric effect in substituted tetrahydropyran [57]

dipolar repulsions are considered as point charges located at the center of each atom (Fig. 1b) [48–50]. More recently, the idea has been suggested by Takahashi, Coheno and Nishio that a non-classical hydrogen bond exists between the axial X group at carbon-1 and the syn-axial hydrogen attached to carbon-5 (Fig. 1c) [51–53]. In this phenomenon (anomeric effect), which is a kind of negative hyperconjugation, the electron density is delocalized from lone-pair orbital to the empty anti-bonding sigma orbital ($n \rightarrow \sigma^*$) (Fig. 1d) [54–56].

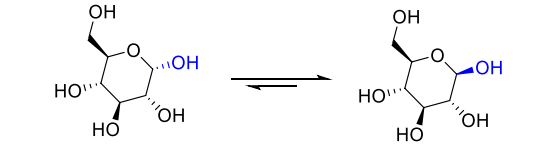
An interesting example of the role of the anomeric effect in the nature is the conversion of α-D-glucopyranose to ß-D-glucopyranose (Scheme 2).

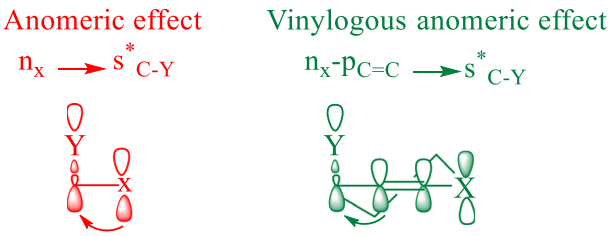
Vinylogous anomeric effect (VAE) is one of the subsets of anomeric effect [58–66]. The VAE occurred when the anomeric effect extended through double bonds. Scheme 3 represents the general modes of anomeric effect and VAE [67].

According to a study by Katritzky, the facile dissociation of the C–N bond of benzotriazole residue in compound A is related to the VAE (Scheme 4) [60].

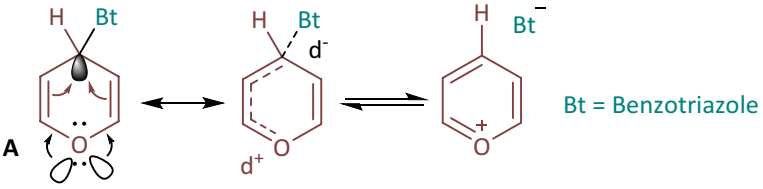
On the other hand, pyridines are excellent compounds that are used in various fields such as pharmacy, agricultural chemicals, materials science. The biological importance of these compounds is clearly known as anti-tumor [69], anti-fungal [70], anti-virial [71] and anti-tuber- culosis [72]. In nature, important compounds such as nicotinic acid (vitamin B3) and pyridoxine (vitamin B6) and many medicinal compounds contain pyridine in their structures (Fig. 2).

Scheme 2 Conversion of α-D-glucopyranose to ß-D-glucopyranose





Scheme 3 Anomeric effect versus VAE



Scheme 4 VAE causes facile C–N bond dissociation of the benzotriazole residue [68]

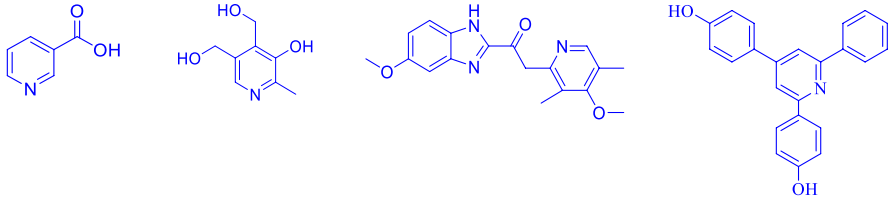
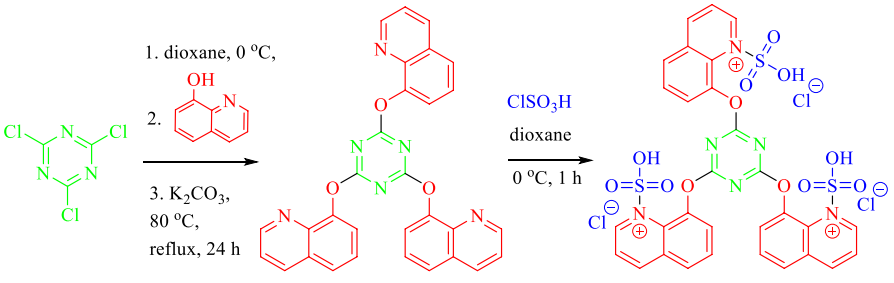


Fig. 2 Structure of some important pyridine derivatives

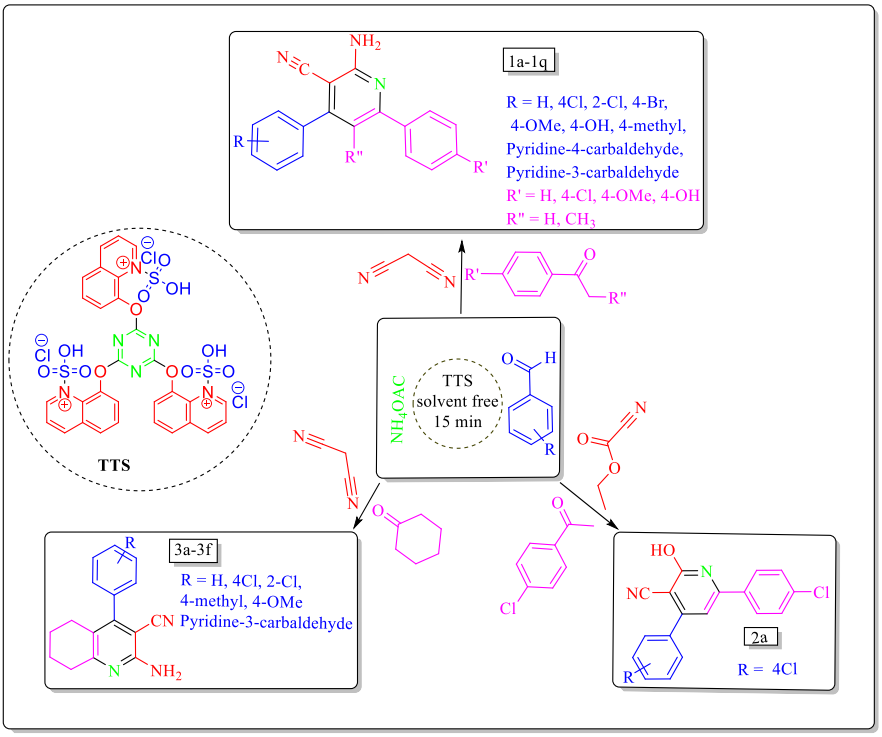
Over the years, various methods have been developed to synthesize pyridines as valuable compounds [73–82]. Many of these methods are not efficient in terms of efficiency, reaction time, and reaction conditions. Therefore, proposing new methods for synthesizing these compounds that have high efficiency and are greener is the aspiration of many. In this paper, to realize this dream and also to present a new and effective method for the synthesis of valuable biological structures using AIL catalysts, we reported the rational design, synthesis, identification and catalytic performance of a new AIL based on 8-hydroxy quinoline called TTS in the synthesis of pyridines via a cooperative vinylogous anomeric-based oxidation. (Schemes 5 and 6).

Experimental

Chemicals were purchased from the Fluka and Merck chemical companies and used without further purification. The reaction progress and purity of the prepared structures were monitored by TLC (silica gel SIL G/UV 254) plates. The FT-IR spectra were recorded on a PerkinElmer Spectrum Version 10.02.00 using KBr pellets. The ^{1}HNMR (300) and ^{13}CNMR (75) spectra were recorded on a Bruker spectrometer (δ in ppm) using DMSO-d_6 as solvent with chemical shifts measured relative to $Si(CH_3)_4$ as an internal standard. Melting points were determined with a Buchi B-545 melting point apparatus in open capillary tubes. Mass spectra were recorded on an AB SCIEX 3200 QTRAP apparatus. Thermogravimetric analyses



Scheme 5 General route toward the synthesis of TTS



Scheme 6 Synthesis of pyridines using TTS as catalyst

were carried out using a Rheometric Scientific STA 1500 TGA apparatus. Elemental mapping analysis and EDS were carried out using a FESEM device model SIGMA VP company ZEISS Germany equipped with detector EDS-mapping-WDS and FBSD company oxford instruments UK.

General procedure for preparation of TTS

Cyanuric chloride (1.84 g, 10 mmol) in dioxane (50 mL) was added slowly to a solution of 8-hydroxyquinolone (4.78 g, 33 mmol) and dioxane (50 mL) in 0 °C and then anhydrous K_2CO_3 (10 g, 70 mmol) was added to resulting solution and was refluxed for 24 h in 80 °C with stirring. The reaction mixture was cooled to room temperature then poured onto filter paper. The almost yellow precipitate that remained on the filter paper was washed several times with distilled water until the precipitate turned white and then washed with ethanol. The resulting precipitate was placed in an oven at 100 °C for 2 h until completely dry. The melting point of the product (2,4,6-Tris[quinolin-8-yloxy]-1,3,5-triazine) which previously reported [83] was 286 °C. In the following, 1.2 mL of chlorosulfonic acid with a density of 1.75 g/mL (18 mmol) was dissolved in 50 cc of dioxane, then by stirring this solution, 2.6 g of the (2,4,6-tris[quinolin-8-yloxy]-1,3,5-triazine) at 0 °C was added to it. After one

hour, the yellow precipitate obtained, which was the new ionic liquid, was removed from the solution and purified with dichloromethane. The general outline of this reaction is shown in the Scheme 5.

General procedure for preparation of pyridine derivatives using TTS

A mixture of ketone derivatives (1 mmol), aldehydes (1 mmol), ammonium acetate (77 mg, 1 mmol, as a precursor for in-situ generation of ammonia), malononitrile (66 mg, 1 mmol) or ethylcyanoacetate (113 mg, 1mmole) and AIL (40 mg) in a 10-mL round-bottomed flask was stirred in an oil-bath at 80 °C. After reaction completion, as monitored by TLC, to separate AIL and other impurities, crude products washed several times with water and warm ethanol. The remaining solid (pure product) was dried in oven.

Results and discussion

The formation of TTS was verified with several skills including FT-IR, EDX, TGA/DTA and elemental mapping are discussed in more detail below.

The IR spectrum of the TTS showed a wide peak in the range 2850–3300 cm^{-1}, which is related to the O–H stretching of SO_3H. The two peaks observed at 1060 cm^{-1} and 1175 cm^{-1} correspond to vibrational modes of N–SO_2 and O–SO_2 bonds. Another peak in 1011 cm^{-1} could be related to the S = O bond (Fig. 3).

By using EDX analysis, the elemental composition of the prepared TTS was explored. As predicted, carbon, oxygen, chlorine, sulfur, and nitrogen were detected in the EDX results (Fig. 4). Therefore, according to the EDX results, the structure of the novel-synthesized AIL is completely inferred.

The thermal behavior of the catalyst was also evaluated using TGA/DTA analysis. The obtained data from this analysis is shown as a plot (Fig. 5). The weight loss up to 175 °C is related to the evaporation of solvents used during the preparation of TTS. Between 300 and 360 °C, about 28% weight loss occurs, which is due to the decomposition of the catalyst acidic groups. Another major weight loss up to 450 °C is related to the decomposition of compound and breaking of C–O bonds. And at higher temperatures, its bonds decompose and a small percentage of it remains. These results indicated the high thermal stability of the TTS.

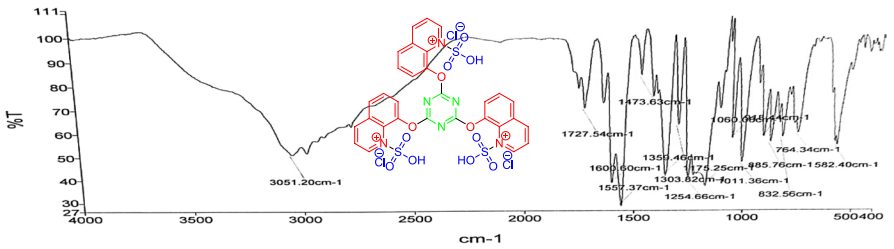


Fig. 3 FT-IR spectrum of TTS

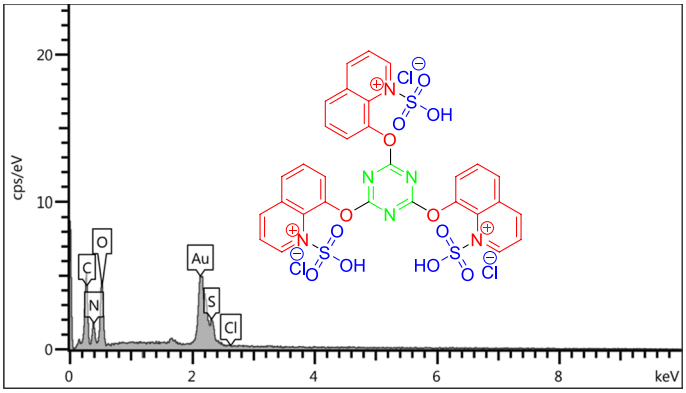


Fig. 4 EDX analysis of TTS

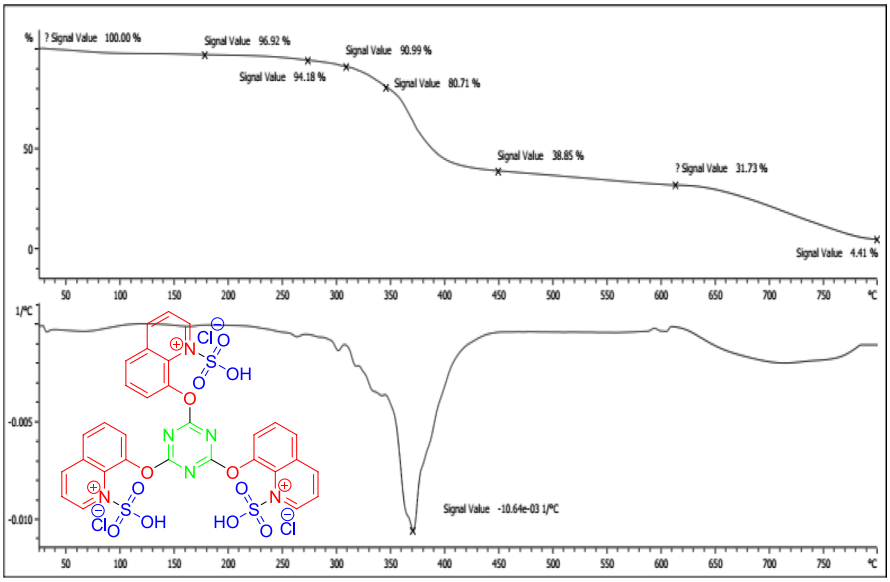


Fig. 5 TGA/DTA plot of TTS

Examination of the elemental mapping analysis showed the presence of C, Cl, O, N and S elements in the catalyst with a good ratio over the catalyst surface (Fig. 6).

After characterization of TTS as a new AIL, we investigated its catalytic performance for the synthesis of pyridines via vinylogous anomeric-based oxidation. To achieve this goal, we initially performed a model reaction with the reaction of 4-chlorobenzaldehyde, 4-chloroacetophenone, malononitrile and ammonium acetate as a source of nitrogen production (raw materials of production 1a) in order to find the best reaction conditions. To find the best results in terms of yield and reaction time, we scrutinized the role of effective parameters such as solvents, reaction

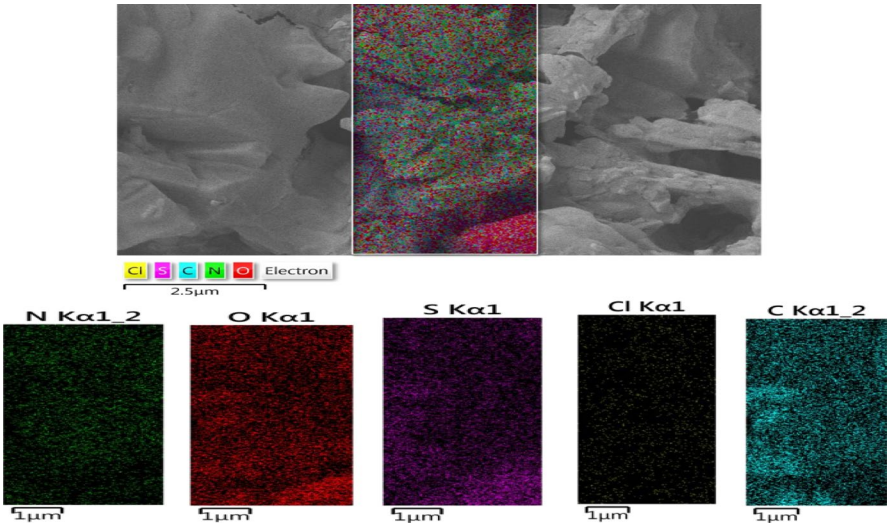


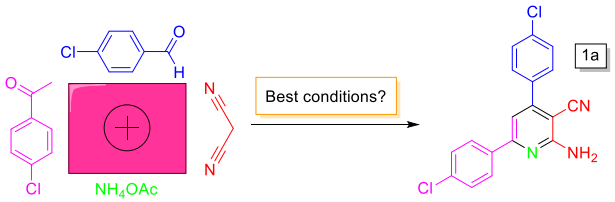
Fig. 6 Elemental mapping images of oxygen (red), nitrogen (green), sulfur (violet), chlorine (gray), carbon (pale green) of TTS. (Color figure online)

temperature, and amount of catalyst to the selected model to produce the desired product (Table 1). The obtained data are summarized in Table 1. The achieved data showed that the best results were obtained when 40 mg of TTS was used at 80 °C (Table 1, entry 4). The reaction was also performed in the absence of catalyst, but no product was formed (Table 1, entry 5).

Next, knowing the optimal reaction conditions, we focused on different substrates for the preparation of pyridine derivatives which the results are given in Table 2. The data show that the desired molecules were obtained in a short reaction time with high efficiency. All synthesized pyridine derivatives were identified by melting point measurements and spectroscopic techniques such as FT-IR, ^{1}HNMR and ^{13}CNMR.

A reasonable mechanism for the synthesis of desired molecule (**1 g**) is showed in Scheme 7. Initially, TTS as a catalyst activates the aromatic carbonyl ketone group which reacts with ammonia and produces intermediate **2** and is converted to **3** after tautomerization. The reaction will continue with the nucleophilic attack of the produced enamine **3** to the Knoevenagel product **4**. In the presence of the TTS, this reaction leads to intermediate **5** and after tautomerization to intermediate **6** which is converted through an intramolecular nucleophilic attack to intermediate **7**. In the next step, after tautomerization, intermediate **7** is converted to intermediate **8**. According to the recent introduced term entitled "anomeric-based oxidation" (ABO) [68, 84–91], intermediate **8**, both endocyclic and exocyclic nitrogen atoms assist hydride departure and releasing of molecular hydrogen (H_2). For approving the above-mentioned idea, the model reaction was performed in the absence of any molecular oxygen, both under argon and nitrogen atmosphere. The obtained data for model reaction under air, argon and nitrogen atmosphere are similar (Table 1, entry 4). (Finally, deprotonation of intermediate 9 generates the desired molecule **1 g**.

Table 1 Optimization of reaction conditions for synthesis of pyridine derivatives[a]



Entry	Solvent	Temperature (°C)	Catalyst loading (mg)	Time (min.)	Yield (%)[b]
1	–	25	40	60	trace
2	–	40	40	60	25
3	–	70	40	25	50
4[c]	–	80	40	15	80
5	–	80	–	60	trace
6	–	80	20	15	trace
7	–	80	60	15	80
8	H_2O	80	40	60	trace
9	C_2H_5OH	80	40	60	30
10	Ethyl acetate	80	40	60	trace
11	*n*-hexane	80	40	60	30
12	$CHCl_3$	80	40	60	trace

[a]Reaction conditions: 4-Chlorobenzaldehyde (140.5 mg, 1 mmol), malononitrile (66 mg, 1 mmol), 4-chloroacetophenone (154.5 mg, 1 mmol) and ammonium acetate (77 mg, 1 mmol)

[b]Isolated yields

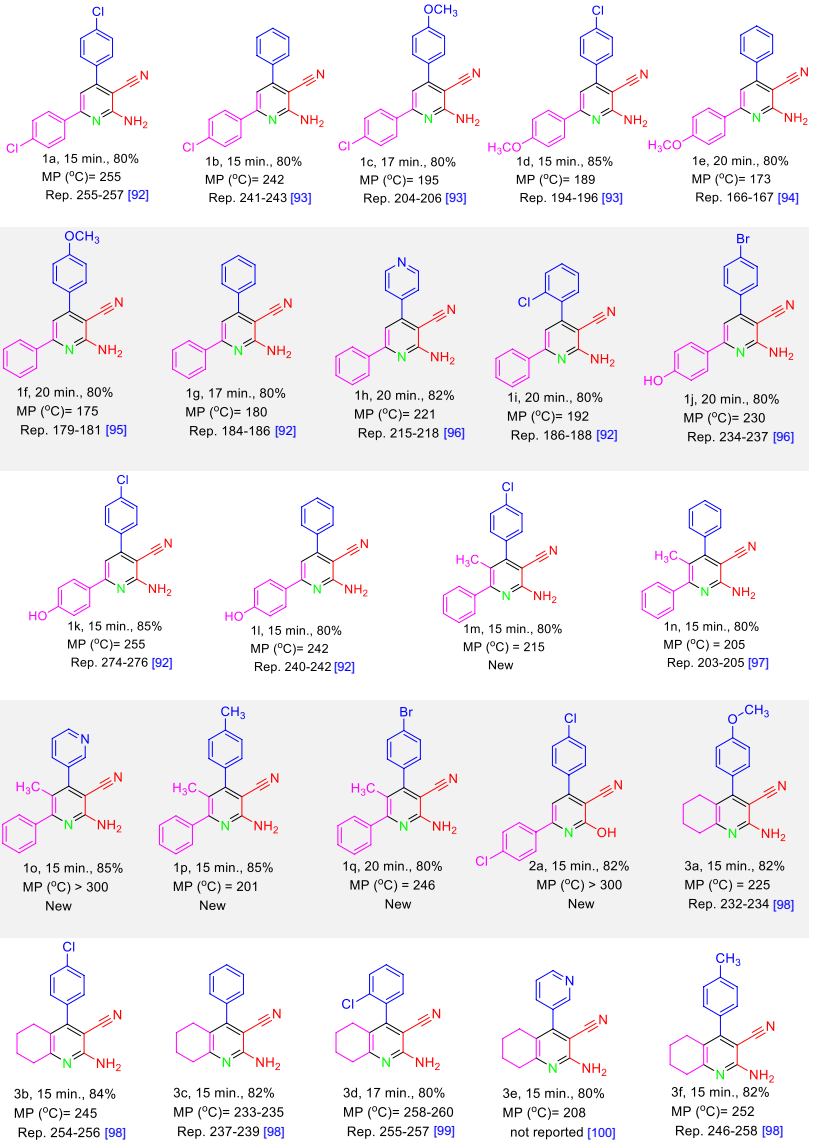
[c]Data for the model reaction under air, argon and nitrogen are similar

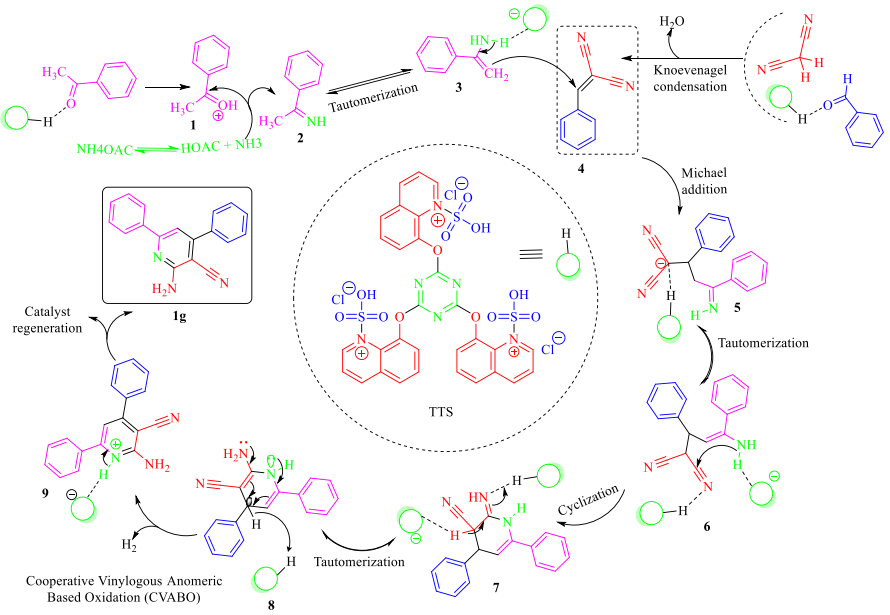
According to Table 3, the method used in this paper for the synthesis of pyridines is superior to many previously reported methods in terms of reaction efficiency, short reaction time, no need for solvent and ease of reaction.

Conclusion

In this work, TTS as an acidic catalyst was designed, synthesized, and identified by several skills including FT-IR, EDX, elemental mapping, TGA/DTA, ^{1}HNMR, ^{13}CNMR and mass spectroscopy. Then, the compound is used to make pyridine derivatives in a four-component reaction. The main advantages of this method include low cost, high efficiency, short reaction time, ease of method and no need for solvent.

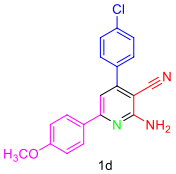
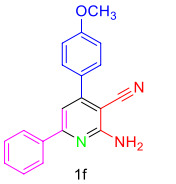
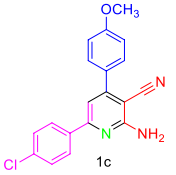
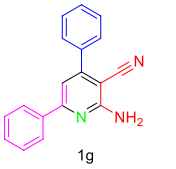
Table 2 Synthesis of pyridine derivatives in the presence of TTS



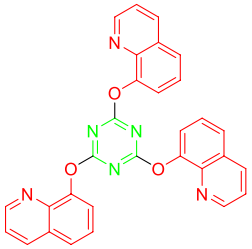


Scheme 7 A reasonable mechanism for the synthesis of desired molecule (1 g) in the presence of TTS

Table 3 Comparison study of prepared catalyst with some other reported catalysts

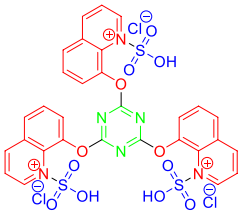
 1d	(1) [Bmim][BF_4], Solvent free, 60 °C, 5 h, 88% [76] (2) Ethyl ammonium nitrate, Solvent free, Reflux, 60 °C, 2.5 h, 90% [77] (3) Fe_3O_4@TiO_2@$O_2PO_2(CH_2)NHSO_3H$, Solvent free, 90 °C, 25 min, 87% [92] (4) Cellulose-SO_3H, H_2O, 60 °C, 2.5 h, 94% [93] (5) TTS, Solvent free, 80 °C, 15 min, 85%, [current work]
 1f	(1) [Bmim][BF_4], Solvent free, 60 °C, 5 h, 78% [76] (2) Ethyl ammonium nitrate, Solvent free, Reflux, 60 °C, 2 h 88%, [77] (3) NMS(5 mol%), Solvent free, 80 °C, 40 min, 91%, [79] (5) Bu_4N^+ Br^-(10 mol%), H_2O, Reflux, 2 h, 73%, [80] (6) TTS, Solvent free, 80 °C, 20 min, 80%, [current work]
 1c	(1) ClO_4^-/Al-MCM-41, Solvent free, 100 °C, 30 min, 79% [81] (2) NMS(5 mol%), Solvent free, 80 °C, 50 min, 85%, [79] (3) Cellulose-SO_3H, H_2O, 60 °C, 3 h, 90% [93] (4) TTS, Solvent free, 80 °C, 17 min, 80%, [current work]
 1g	(1) Bu_4N^+ Br^-(10 mol%), H_2O, Reflux, 2 h, 92%, [80] (2) Fe_3O_4@TiO_2@$O_2PO_2(CH_2)NHSO_3H$, Solvent free, 90 °C, 20 min, 90% [92] (3) [BBIM]Br, Solvent free, 28 °C, 5 h, 78%, [82] (4) [BBIM]BF_4, Solvent free, 28 °C, 4.5 h, 81%, [82] (5) Cellulose-SO_3H, H_2O, 60 °C, 2.5 h, 95%, [93] (6) TTS, Solvent free, 80 °C, 17 min, 80%, [current work]

Selected spectral data



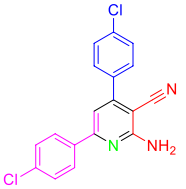
2,4,6-Tris(quinolin-8-yloxy)-1,3,5-triazine

M.p. 286 °C. FT-IR (KBr, ν, cm^{-1}): 3068.5, 1579.12, 1554.95, 1529.86, 1499.83, 1469.92, 1362.71, 1239.89, 1292.71, 1165.66, 115.32, 944.48, 792.62, 755.05. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.83(d, $J=3$ Hz, 3H), 8.44–8.32 (m, 3H), 7.96–7.92 (m, 3H), 7.85–7.47 (m, 9H), ^{13}C NMR (75 MHz, DMSO-d_6) δ 174.13, 151.02, 147.54, 140.45, 136.54, 129.46, 126.76, 126.66, 122.62, 121.45.



8,8',8"-((1,3,5-triazine-2,4,6-triyl)tris(oxy))Tris(1-sulfoquinolin-1-ium) chloride

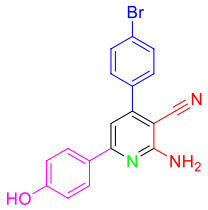
M.p. 91–93 °C. FT-IR (KBr, ν, cm^{-1}): 3051, 1727, 1600, 1557, 1359, 1175, 1060, 1011, 582, ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.19 (s, 3H, SO_3H), 9.15 (dd, $J=20$ Hz, $J=6$ Hz, 6H), 8.10 (dd, $J=9$ Hz, $J=6$ Hz, 3H), 7.79 (d, $J=3$ Hz, 6H), 7.50 (t, $J=3$ Hz, 3H), ^{13}C NMR (75 MHz, DMSO-d_6) δ 150.41, 148.70, 147.02, 144.80, 130.99, 130.23, 129.09, 122.92, 119.04, 116.53, MS: ESI-mass: m/z = 860.



2-Amino-4,6-bis(4-chlorophenyl)nicotinonitrile

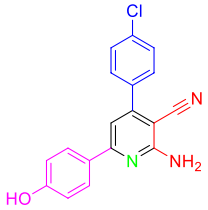
M.p. 255 °C. FT-IR (KBr, ν, cm^{-1}): 3503, 3395.28, 2205.84, 1609.11, 1581, 1545.87, 1493.83, 1093.69, 1013, 823.05. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.17 (d, $J=6$ Hz, 2H), 7.72 (d, $J=6$ Hz, 2H), 7.64 (d, J = 9 Hz, 2H), 7.57 (d, J = 9 Hz, 2H), 7.32 (s, 1H), 7.13 (bs, 2H, NH_2), ^{13}C NMR (75 MHz, DMSO-d_6) δ 161.24,

157.88, 154.19, 136.66, 136.06, 135.51, 135.07, 130.70, 129.45, 117.27, 109.53, 87.29.



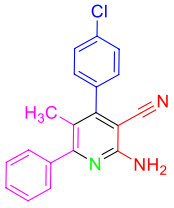
2-Amino-4-(4-bromophenyl)-6-(4-hydroxyphenyl)nicotinonitrile

M.p. 230 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.97 (s, 1H, OH), 8.03 (d, J = 9 Hz, 2H), 7.78 (d, J = 9 Hz, 2H), 7.64 (d, J = 9 Hz, 2H), 7.19 (s, 1H), 6.96 (s, 2H, NH_2), 6.88 (d, J = 9 Hz, 2H), ^{13}C NMR (75 MHz, DMSO-d_6) δ 161.25, 160.12, 159.28, 153.75, 136.85, 132.14, 130.95, 129.48, 128.72, 123.55, 117.64, 115.90, 108.50, 85.47.



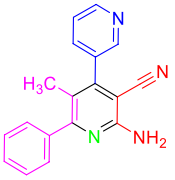
2-Amino-4-(4-chlorophenyl)-6-(4-hydroxyphenyl)nicotinonitrile

M.p. 255 °C. FT-IR (KBr, ν, cm^{-1}): 3497.6, 3463.2, 3354.64, 2207.95, 1566.47, 1547.38, 1231.97, 1093.97, 819.86, 617.95. ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.98 (s, 1H, OH), 8.03 (d, J = 9 Hz, 2H), 7.71 (d, J = 9 Hz, 2H), 7.64 (d, J = 9 Hz, 2H), 7.19 (s, 1H), 6.95 (bs, 2H, NH_2), 6.88 (d, J = 9 Hz, 2H), ^{13}C NMR (75 MHz, DMSO-d_6) δ 161.23, 160.10, 159.26, 153.71, 136.48, 134.85, 130.71, 129.48, 129.22, 128.72, 117.64, 115.90, 108.57, 85.55.



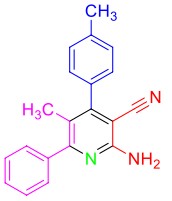
2-Amino-4-(4-chlorophenyl)-5-methyl-6-phenylnicotinonitrile

M.p. 215 °C. FT-IR (KBr, ν, cm^{-1}): 3471.8, 3276.6, 3144.95, 2214.4, 1627.67, 1556.21, 1492.12, 1090.74, 698.32. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.62 (d, J = 9 Hz, 2H), 7.50–7.44 (m, 7H), 6.82 (bs, 2H, NH_2), 1.83 (s, 3H, CH_3), ^{13}C NMR (75 MHz, DMSO-d_6) δ 162.05, 158.50, 154.48, 140.33, 136.38, 134.08, 130.86, 129.23, 128.90, 128.43, 116.98, 89.41, 17.17.



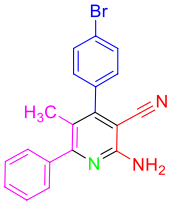
2'-Amino-5'-methyl-6'-phenyl-[3,4'-bipyridine]-3'-carbonitrile

M.p > 300 °C. FT-IR (KBr, ν, cm^{-1}): 3468.9, 3288, 3154.06, 2214.4, 1632.55, 1556.77, 1438.37, 1102.39, 769.23, 702.47, 616.21. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.70 (d, J = 6 Hz, 1H), 8.63 (s, 1H), 7.91 (d, J = 6 Hz, 1H,), 7.61–7.58 (m, 1H), 7.57–7.45 (m, 5H), 6.87 (bs, 2H, NH_2), 1.85 (s, 3H, CH_3), ^{13}C NMR (75 MHz, DMSO-d_6) δ 162.19, 158.56, 152.26, 150.32, 149.18, 140.23, 136.81, 133.49, 129.25, 128.97, 128.46, 124.10, 117.45, 116.94, 89.59, 17.20.



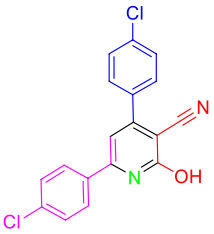
2-Amino-5-methyl-6-phenyl-4-(*p*-tolyl)nicotinonitrile

M.p. 201 °C. FT-IR (KBr, ν, cm^{-1}): 3477.5, 3291, 3139.5, 2211.37, 1633.49, 1557.66, 1371.6, 1097.76, 773.19, 707.8, 615.15. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.52–7.43 (m, 5H), 7.34 (d, J = 6 Hz, 2H),7.27 (d, J = 6 Hz, 2H), 6.72 (bs, 2H, NH_2), 2.38 (s, 3H, CH_3), 1.82 (s, 3H, CH_3), ^{13}C NMR (75 MHz, DMSO-d_6) δ 161.86, 158.53, 155.81, 150.42, 144.51, 140.47, 138.61, 134.59, 130.02, 129.68, 129.22, 128.83, 128.73, 128.41, 117.19, 89.75, 21.34, 17.22.



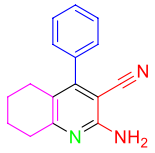
2-Amino-4-(4-bromophenyl)-5-methyl-6-phenylnicotinonitrile

M.p. 170–180 °C. FT-IR (KBr, ν, cm^{-1}): 3471.8, 3146.12, 2212.00, 1625.96, 1555.12, 1489.65, 1439.63, 1247.49, 1070.98, 1007.31, 826.99, 769.92, 697.94, 615.49, ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.75 (d, J = 6 Hz, 2H), 7.52–7.43 (m, 5H), 7.39 (d, J = 9 Hz, 2H), 6.82 (bs, 2H, NH_2), 1.83 (s, 3H, CH_3), ^{13}C NMR (75 MHz, DMSO-d_6) δ 162.08, 158.54, 154.48, 150.56, 140.31, 136.73, 132.17, 131.08, 129.23, 128.89, 128.42, 122.78, 117.08, 117.01, 89.37, 17.17.



4,6-Bis(4-chlorophenyl)-2-hydroxynicotinonitrile

M.p > 300 °C. FT-IR (KBr, ν, cm^{-1}): 3021, 2843, 2214.4, 1630.97, 1493.02, 1225.50, 1091.08, 1013.29, 819.26, 563.33. ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.29 (bs, 1H, OH), 7.96 (d, $J = 9$ Hz, 2H), 7.77 (d, $J = 9$ Hz, 2H), 7.65 (d, $J = 9$ Hz, 2H), 7.60 (d, $J = 9$ Hz, 2H), 6.90 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 162.65, 158.66, 151.29, 136.55, 135.83, 135.19, 131.85, 130.69, 130.09, 129.37, 129.31, 116.75, 107.12, 98.72.



2-Amino-4-phenyl-5,6,7,8-tetrahydroquinoline-3-carbonitrile

M.p. 233–235 °C. FT-IR (KBr, ν, cm^{-1}): 3422.55, 3149.15, 2927.36, 2214.15, 1646.76, 1555.24, 1420.68, 1253.24, 1095.21, 756.77, 703.67, 614.65.^{1}H NMR (300 MHz, DMSO-d_6) δ 7.50–7.44 (m, 3H), 7.29 (d, $J = 6$ Hz, 2H), 6.58 (bs, 2H, NH_2), 2.70 (t, $J = 6$ Hz, 2H, CH_2), 2.19 (t, J = 6 Hz, 2H, CH_2), 1.73–1.71 (m, 2H, CH_2), 1.60–1.58 (m, 2H, CH_2), ^{13}C NMR (75 MHz, DMSO-d_6) δ 161.43, 158.38, 154.42, 136.85, 129.05, 128.99, 128.52, 118.79, 117.14, 88.52, 33.29, 26.33, 22.92, 22.57.

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