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Title: One-pot, solvent-free and efficient synthesis of 2,4,6-triarylpyridines catalyzed by nano-titania-supported sulfonic acid as a novel heterogeneous nanocatalyst

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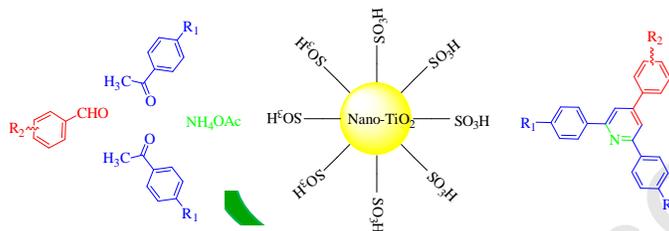
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Graphical Abstract

One-pot, solvent-free and efficient synthesis of 2,4,6-triarylpyridines catalyzed by nano-titania-supported sulfonic acid as a novel heterogeneous nanocatalyst

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Nano-titania-supported sulfonic acid as an efficient and recyclable heterogeneous nanocatalyst is reported for the synthesis of 2,4,6-triarylpyridines under solvent-free conditions. One new compound is reported too.

Original article

One-pot, solvent-free and efficient synthesis of 2,4,6-triarylpyridines catalyzed by nano-titania-supported sulfonic acid as a novel heterogeneous nanocatalyst

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ABSTRACT

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Nano titania-supported sulfonic acid (n-TSA) has found to be a highly efficient, eco-friendly and recyclable heterogeneous nanocatalyst for the solvent-free synthesis of 2,4,6-triarylpyridines through one-pot three-component reaction of acetophenones, aryl aldehydes and ammonium acetate. This reported method illustrates several advantages such as environmental friendliness reaction conditions, simplicity, short reaction time, easy work up, reusability of catalyst and high yields of the products. One new compound is reported too. Furthermore, the catalyst could be recycled after a simple work-up, and reused at least six times without substantial reduction in its catalytic activity.

1. Introduction

In the last two decades, multicomponent reactions (MCRs) have been widely used in organic synthesis due to their efficacy for the generation of heterocyclic compounds in a single synthetic step [1]. These reactions represent very powerful chemical technology procedures from both economical and synthetic points of view and they are one of the most influential techniques in green chemistry, industrial chemistry and the modern drug discovery process [2]. Therefore, the discovery of novel MCRs is an interesting topic for synthetic chemistry researchers.

Recently, solid-supported heterogeneous catalysts have gained considerable interest in organic synthesis because of their unique properties such as high efficiency due to more surface area, more stability, reusability, low toxicity and ease of handling [3-8]. We have recently reported nano titania-supported sulfonic acid (n-TSA) [9], as an effective heterogeneous acidic nanocatalyst for the promotion of a wide range of organic reactions as for its Lewis and Bronsted acidity features. Ease of preparation, simple work-up procedures and improved product yields, facile purification, shorter reaction times, mild reaction conditions and recyclability of the catalyst are the main superiorities of n-TSA.

Pyridine ring systems, particularly 2,4,6-triarylpyridines represent an important class of heterocyclic compounds because of their unique position in medicinal chemistry [10, 11]. Moreover, they are prominent synthons in supramolecular chemistry, with their π -stacking ability along with directional H-bonding capacity [12, 13]. In addition, the excellent thermal stabilities of these pyridines have instigated a growing interest for their use as monomeric building blocks in thin films and organometallic polymers [14].

Since, Krohnke's original report on the synthesis of 2,4,6-triarylpyridines [15], there has been a plethora of research targeting their syntheses [16, 17]. Recently, the synthetic approach to 2,4,6-triarylpyridines involves cyclo-condensation reaction of acetophenones, benzaldehydes and ammonium acetate in the presence of different catalysts under heating condition or sonication and microwave irradiation [18-22].

Wide variety of 2,4,6-triarylpyridine chemical and pharmacological applications, encouraged us to develop and validate an efficient protocol for their synthesis. Herein, we have reported nano titania-supported sulfonic acid catalyzed synthesis of 2,4,6-triarylpyridines under solvent-free conditions.

2. Experimental

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Chemicals were purchased from the Merck chemical companies. Thin-Layer Chromatography (TLC) on commercial plates of silica gel 60 F254 was used to monitor the progress of reactions. The products were characterized by FT-IR spectra, ^1H NMR and ^{13}C NMR. FT-IR spectra were recorded on Shimadzu FT-IR 8400 instrument. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker Advance Spectrometer 300 MHz and 75 MHz respectively, using CDCl_3 as solvent. The chemical shifts are expressed in parts per million (ppm) and tetramethylsilane (TMS) was used as an internal reference. Melting points were recorded on a THERMO SCIENTIFIC 9100 apparatus.

2.1. General procedure for the synthesis of catalyst (n-TSA)

Chlorosulfonic acid (1 mL, 15 mmol) was added dropwise to a suspension of powdered nano TiO_2 (4 g) in dry CH_2Cl_2 (20 mL) over a period of 30 min while the mixture was stirred slowly in an ice bath. The mixture was stirred for 30 min at room temperature until HCl evolution was seized. Then, the CH_2Cl_2 was removed under reduced pressure and the solid powder was washed with ethanol (10 mL) and dried at 70°C . n-TSA was obtained as a white solid powder [9].

The mmol of H^+ per gram of catalyst was also evaluated. For this purpose, the surface acidic protons of nano- $\text{TiO}_2\text{-SO}_3\text{H}$ (100 mg) were ion-exchanged with a saturated solution of NaCl (10 mL) by sonicating. This process was repeated twice more, yielding 30 mL of proton-exchanged brine solution. Therefore, to determine the loading of acid sites on the synthesized catalyst the obtained solution titrated with NaOH (0.1 mol/L) solution in the presence of phenol red indicator solution or pH meter. The amounts of acidic protons found to be $4.5\text{ mmol}\cdot\text{g}^{-1}$ of n-TSA. This finding means the effective density of the acid sites.

The catalyst was characterized in our previously published paper by the X-ray diffraction (XRD), scanning electron microscopy (SEM), FT-IR spectroscopy, thermal gravimetric analysis (TGA) and the acid strength of n-TSA was determined by the Hammett acidic function too [9].

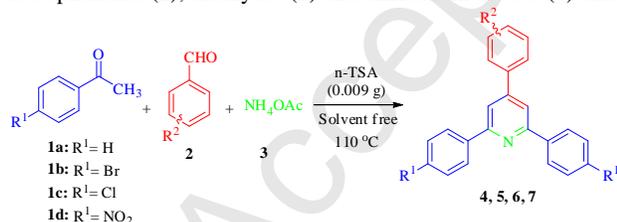
2.2. General procedure for the synthesis of 2,4,6-triarylpyridine derivatives

A mixture of acetophenones (2 mmol), aromatic aldehydes (1 mmol), ammonium acetate (1.5 mmol) and 0.009 g of n-TSA was stirred at 110°C under solvent-free condition for an appropriate time. After completion of the reaction (monitored by TLC), the reaction mixture was cooled, eluted with hot ethanol (2 mL) and was centrifuged to separate the catalyst. The title compounds were obtained in their crystalline forms by recrystallization of ethanol solution.

2,6-Bis(4-bromophenyl)-4-(*p*-tolyl)pyridine (**5c**): Light green crystal; mp: $236\text{-}240^\circ\text{C}$; IR (KBr, cm^{-1}) ν_{max} : 3028, 1601, 1577, 1516, 1489; ^1H NMR (300 MHz, CDCl_3): δ 2.46 (s, 3H), 7.33 (d, 2H, $J = 8.12$ Hz), 7.60 (m, 6H), 7.80 (m, 2H), 8.05 (dd, 4H, $J = 7.66, 4.02$ Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 21.3, 116.8, 123.6, 126.9, 128.6, 129.9, 131.8, 135.6, 138.2, 139.3, 150.3, 156.3.

3. Results and discussion

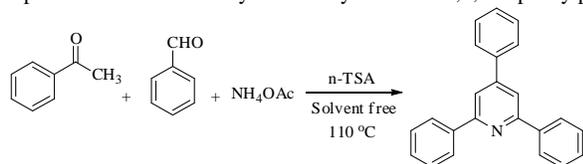
Considering our researches toward evaluating the catalytic activity of n-TSA for the synthesis of organic compounds [9, 23], we have investigated the synthesis of 2,4,6-triarylpyridines (**4-7**) *via* one-pot, three-component cyclo-condensation reaction of acetophenones (**1**), aldehydes (**2**) and ammonium acetate (**3**) under solvent-free conditions (Scheme 1).



Scheme 1. Synthesis of 2,4,6-triarylpyridine derivatives by n-TSA.

To choose the most appropriate condition in this reaction and to understand the influence of different variables, several experiments were studied. Initially, we optimized the amount of catalyst in order to find the required catalyst load. The obtained results are listed in Table 1.

Table 1
Optimum amount of catalyst on the synthesis of 2,4,6-triphenylpyridine.^a



Entry	Catalyst (g)	Yield (%) ^b	TON ^c	TOF ^d (h ⁻¹)
1	0	65	-	-
2	0.002	73	58.4	29.2
3	0.004	85	34	17
4	0.009	93	16.53	8.26
5	0.012	92	12.27	6.13
6	0.016	91	9.1	4.55
7	0.020	91	7.28	3.64

^a Reaction conditions: acetophenone (2 mmol), benzaldehyde (1 mmol), NH₄OAc (1.5 mmol) at 110 °C under solvent-free conditions, reaction time: 2 h.

^b Isolated yields.

^c TON= mmol of product per mmol of catalyst.

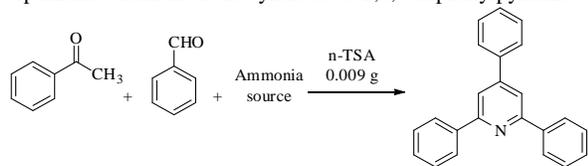
^d TOF= TON/time.

As indicated in Table 1, the best yield was obtained in the presence of 0.009 g catalyst, which is enough to carry out the reaction efficiently (Table 1, entry 4).

In the next step, the effect of temperature, solvent and ammonia source was examined over the reaction and the obtained results are shown in Table 2.

Table 2

Optimum condition on the synthesis of 2,4,6-triphenylpyridine.^a



Entry	Temp (°C)	Solvent	Ammonia source	Yield (%) ^b
1	60	-	NH ₄ OAc	0
2	70	-	NH ₄ OAc	20
3	80	-	NH ₄ OAc	51
4	90	-	NH ₄ OAc	75
5	100	-	NH ₄ OAc	82
6	110	-	NH ₄ OAc	93
7	120	-	NH ₄ OAc	90
8	110	CH ₂ Cl ₂	NH ₄ OAc	10
9	110	CH ₃ CN	NH ₄ OAc	22
10	110	CHCl ₃	NH ₄ OAc	31
11	110	H ₂ O	NH ₄ OAc	15
12	110	EtOH	NH ₄ OAc	70
13	110	PEG-400	NH ₄ OAc	81
14	110	-	NH ₄ Cl	10
15	110	-	NH ₄ Br	20
16	110	-	NH ₄ I	15
17	110	-	(NH ₄) ₂ SO ₄	0
18	110	-	(NH ₄) ₂ CO ₃	50

^a Reaction conditions: acetophenone (2 mmol), benzaldehyde (1 mmol), ammonia source (1.5 mmol), n-TSA (0.009 g), reaction time: 2 h.

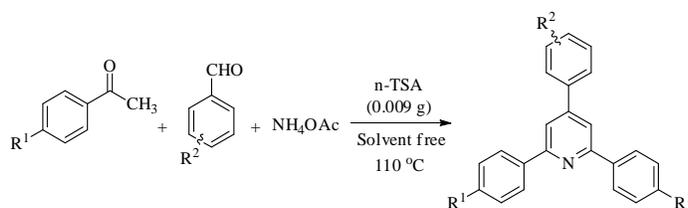
^b Isolated yields.

As can be seen in Table 2, the product yield increased as the reaction temperature was raised at 110 °C and the product was obtained in high yield which was considered as the optimum temperature (Table 2, entry 6), but at higher temperature the yield was decreased (Table 2, entry 7) due to side reactions monitored by TLC. On the other hand, neither polar nor non-polar solvents are suitable for this reaction (Table 2, entries 8-13) and the best yield was obtained under solvent-free condition (Table 2, entry 6), which is due to the appropriate interaction between the catalyst and solvent. Eventually, the effect of various ammonia sources on yield of the product was shown that the maximum yield was obtained for NH₄OAc (Table 2, entry 6), while other ammonia sources required longer reaction times and produced lower yields (Table 2, entries 14-18).

To develop the scope of the reaction, a wide range of aldehydes and acetophenones was subjected to n-TSA-catalyzed reaction under the optimized conditions (Table 3).

Table 3

Synthesis of 2,4,6-triarylpyridine derivatives in the presence of nano-TiO₂-SO₃H.^a



Entry	R ¹	R ²	Time (min)	Product	Yield (%) ^b	Melting point (°C)
1	H	4-H	120	4a	93	135-138
2	H	4-Cl	100	4b	95	123-124
3	H	4-Br	90	4c	94	165-166
4	H	4-OH	140	4d	84	196-198
5	H	4-NO ₂	80	4e	87	194-195
6	H	4-CH ₃	135	4f	88	127-129
7	H	4-OCH ₃	150	4g	82	100-101
8	H	2-Cl	105	4h	94	115-117
9	H	4-N(CH ₃) ₂	130	4i	87	135-137
10	Br	4-H	100	5a	95	104-106
11	Br	4-Cl	110	5b	96	>200
12	Br	4-CH ₃	120	5c ^c	92	236-240
13	Br	3-NO ₂	80	5d	93	>200
14	Cl	4-H	120	6a	88	123-125
15	Cl	2-Cl	110	6b	89	169-171
16	Cl	4-CH ₃	125	6c	87	202-204
17	Cl	4-OCH ₃	130	6d	83	187-188
18	Cl	4-N(CH ₃) ₂	120	6e	84	140-142
19	NO ₂	4-H	100	7a	90	316-318
20	NO ₂	4-CH ₃	110	7b	88	312-313
21	NO ₂	4-OCH ₃	115	7c	87	143-145

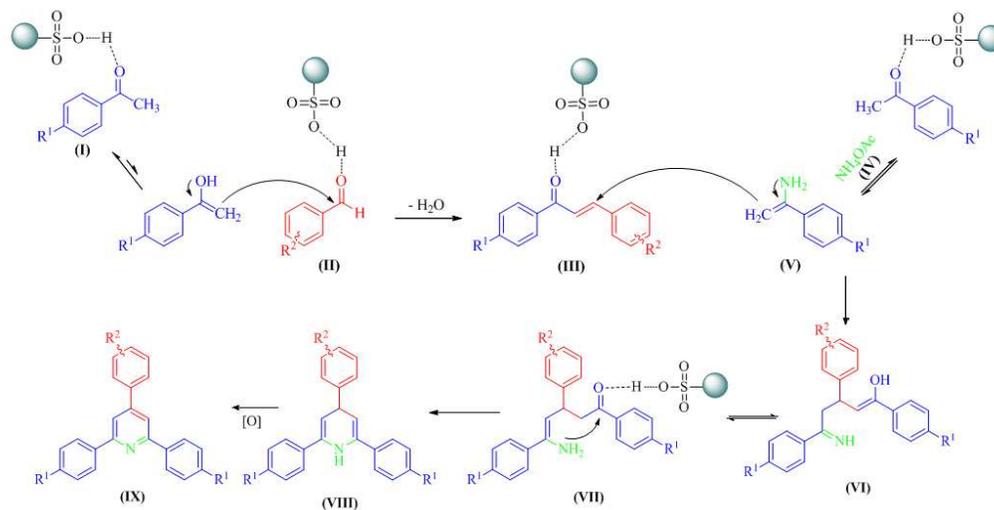
^a Reaction conditions: acetophenone (2 mmol), aldehyde (1 mmol), ammonium acetate (1.5 mmol), n-TSA (0.009 g) at 110 °C under solvent-free conditions.

^b Isolated yields.

^c New compound.

In all cases, aromatic aldehydes with substituents carrying either electron-donating or electron-withdrawing groups reacted successfully and gave the products in good yields (Table 3). It was found that aromatic aldehydes with electron-withdrawing groups (Table 3, entries 2, 3, 5, 8, 11, 13, 15) reacted faster than those with electron-donating groups (Table 3, entries 4, 6, 7, 9, 12, 16-18, 20, 21), as would be expected [24, 25]. These results justified one more time the efficiency of n-TSA.

The proposed mechanism for the formation of 2,4,6-triarylpyridines is depicted in Scheme 2. The reaction involves four major stages: Aldol condensation, Michael addition, cyclization, and oxidation. Initially, acetophenone (**I**) in the presence of nano-TiO₂-SO₃H is converted into its enol form which gives nucleophilic addition to the arylaldehyde (**II**), which is activated by the catalyst, to afford aldol condensation product (**III**). Then, a molecule of acetophenone is condensed with an ammonia source (**IV**) and enamine (**V**) is formed. SO₃H group of n-TSA enhances the electron deficiency on carbonyl group of (**III**) which easily could be attacked by (**V**) in a Michael addition reaction to afford intermediate (**VI**). The following cyclisation provides dihydropyridine (**VIII**). Finally, air oxidation gives the final product (**IX**). As indicated in Scheme 2, the SO₃H groups of n-TSA plays principal role in the catalytic activity of the catalyst and promotion of the reaction rate.



In order to exhibit the merit of the present work, our results are compared with some other previously reported studies in the Table 4.

Table 4

Comparison n-TSA with other reported catalysts in the synthesis of 2,4,6-triphenylpyridine.

Entry	Catalyst (amount mol%)	Condition	Time (h)	Yield (%)	TON ^b	TOF ^c (h ⁻¹)	Reference
1	MgAl ₂ O ₄ (7)	120 °C, solvent-free	3	85	12.14	4.05	[26]
2	AlPO ₄ (10)	120 °C, solvent-free	4	87	8.70	2.17	[27]
3	TBAHS ^a (30)	120 °C, solvent-free	5	70	2.33	0.47	[28]
4	[HO ₃ S(CH ₂) ₄ MIM][HSO ₄] (20)	120 °C, solvent-free	3	88	4.40	1.47	[24]
5	ZrOCl ₂ (15)	100 °C, solvent-free	4	91	6.07	1.52	[19]
6	n-TSA (5.62)	110 °C, solvent-free	2	93	16.53	8.26	This work

^a Trichloroisocyanuric acid.

^b TON= mmol of product per mmol of catalyst.

^c TOF= TON/time.

As shown in Table 4, n-TSA can act as an effective catalyst with respect to the reaction time, yield of the product, TON (turnover number) and TOF (turnover frequency). Moreover, it can be recovered and reused for several times.

The principle advantage of the use of heterogeneous catalysts in organic transformations is their reusability. For this purpose, after completion of the reaction, the reaction mixture was cooled, eluted with hot ethanol (2 mL) and was centrifuged to filter the catalyst. The catalyst was then washed with ethanol, dried at 50 °C and used directly for the synthesis of 2,4,6-triphenylpyridine. The recovered n-TSA was reused for 6 consecutive reactions and obtained the yield 90%-93%. This indicates that n-TSA does not lose its activity and can be recyclable (Fig. 1).

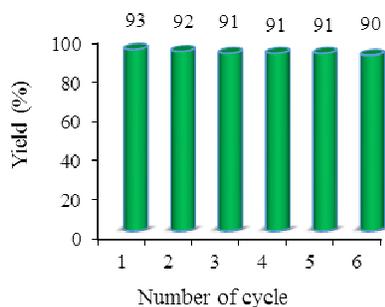


Fig. 1. Reusability of n-TSA for the synthesis of 2,4,6-triphenylpyridine.

The particle size of the recovered catalyst was confirmed by the scanning electron microscopy of the six-time reused catalyst, which clearly demonstrated the same particle size (spherical powder with average size of 35-60 nm) and high stability of the nano TiO₂-based solid acid catalyst (Fig. 2).

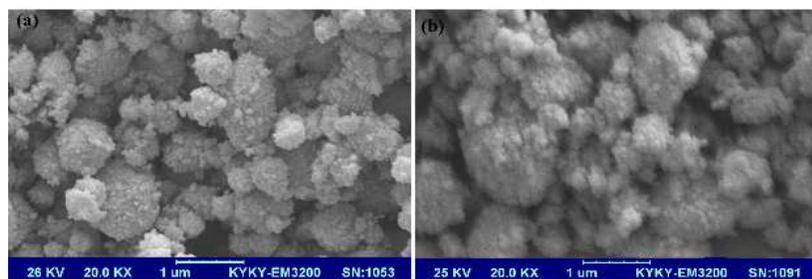


Fig. 2. SEM images of n-TSA before use (a) and after reuse six times (b).

4. Conclusion

In summary, an efficient and rapid route for the synthesis of 2,4,6-triarylpyridines under solvent-less conditions is reported. Operational simplicity, short reaction time, simple work-up without column chromatographic purification, reusability of the catalyst, tolerance of various functional groups, excellent yields of products and solvent free conditions are the advantages of this protocol. Moreover, one new compound is reported.

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