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Sulfamic Acid: An Efficient and Recyclable Solid Acid Catalyst for the Synthesis of Quinoline-4-Carboxylic Acid Derivatives in Water

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Abstract

A simple, cost-effective, environmentally, and convenient procedure for the synthesis of quinoline-4-carboxylic acid derivatives is described through a one-pot MCR condensation of pyruvic acid, various aniline derivatives, and differently substituted aryl aldehydes in the presence of sulfamic acid (NH_2SO_3H) (SA) as an efficient and recyclable catalytic system under mild reaction conditions in water.

Keywords: Quinoline-4-caboxylic acid derivatives; One-pot MCR; Sulfamic acid; Recyclable catalyst; Green chemistry

Introduction

Quinoline [1] 1-aza-napthalene and benzo[b]pyridine are nitrogen containing heterocyclic aromatic compounds. Quinolines are very important compounds due to their wide spectrum of biological activities behaving as anti-malarial, anti-bacterial, anti-fungal, anti-asthmatic, anti-hypertensive, anti-inflammatory, anti-platelet activity [2-9]. In addition quinolines have been employed in the study of bioorganic and bio organo-metallic processes [10,11]. Considering the significant applications in the fields of medicinal, bioorganic, industrial, and synthetic organic chemistry, there has been tremendous interest in developing efficient methods for the synthesis of quinolines. Some derivatives of such as quinoline-4-carboxylic acid elicited profound changes in the morphology of typical tips of *Botrytis cinerea* [12] Quinoline-4-carboxylic acids are one of the most important series of quinoline derivatives because they exhibit a wide variety of medicinal effects and are applied as active components in industrial antioxidants [13,14]. Meanwhile, quinoline-4-carboxylic acids are the key precursors for the synthesis of other useful quinoline derivatives [15]. Despite remarkable efforts in the last decade [16-19] the development of effective methods for the synthesis of quinoxaline ring is still an important challenge and much in demands. In recent years, many methods for the synthesis of these quinoline acids have successively been reported. The conventional synthesis involves the Pfitzinger reaction [20,21]. Doebner reaction [22,23], Friedlander and Combes methods [24-31]. However, these synthetic methods require expensive and hazardous solvents and chemicals, as well as harsh reaction condition. Therefore, the development of simple, convenient, and environmentally benign approaches for the synthesis of quinolines is still desirable. In recent years, the use of solid acids as heterogeneous catalysts has received tremendous interest in various areas of organic synthesis [32-34]. Heterogeneous solid acids are advantageous over conventional homogeneous acid catalysts as they can be easily recovered from the reaction mixture by simple filtration and can be reused after activation or without activation and more importantly without appreciable lose in activities. SA has emerged as a substitute for conventional Bronsted- and Lewis acid catalysts. This catalyst is an amino acid containing sulfur element with mild acidity. It is fast coming up as a stable, white odorless crystalline, commercially available, also not volatile and corrosive, thus can be considered as green catalyst in organic synthesis [35-37]. Interestingly, sulfamic acid exists not only in its amino sulfonic acid form, but also as $H_3N^+SO^{-3}$ zwitterionic units [38] immiscible with commonly employed non-polar organic solvents [35]. Also, it is a white crystalline solid [39]. In recent years, SA has been extensively used as an efficient heterogeneous catalyst for acid catalyzed reactions, such as, acetalization, [40] esterification, [41-43] functional group protections and deprotections [44] the Michael addition [45] amino Diels–Alder reactions [46], Biginelli condensations [47] and Beckmann rearrangement [48].

As the aforesaid conditions are not compatible with heat- or acid-sensitive substrates, there is a need to develop an effective synthesis of quinoxalines employing more ecofriendly conditions and catalysts [49-60]. With considering green chemistry principles, especially using water greenest and most abundant solvent [61-70]. We have recently reviewed the application of Doebner reaction in synthesis of heterocycles including quinolone-4-carboxylic acids [71]. We also frequently used Sulfamic acid as an efficient catalyst in different organic transformations [72-80] and published a review highlighting the application of Sulfamic acid in organic synthesis [81,82]. Armed with these experiences, in response to the need for the facile, efficient and green synthesis of quinolone-4-carboxylic acid derivatives, herein we wish to report the high yielding, one pot MCRs synthesis of this heterocyclic *via* condensation of pyruvic acid, various amines and aryl benzaldehyde in the presence of SA as a relatively inexpensive and available catalyst in water under mild reaction conditions. These eco-friendly protocols offer several advantages such as green, convenient and cost-effective procedures with high yield, shorter reaction time, simpler work-up, recovery, and reusability of solid acid heterogeneous catalyst (SA) in subsequent reactions.

Results and Discussion

To optimize the reaction conditions, a mixture of pyruvic acid (1.2 mmol), aniline (1.1 mmol), and benzaldehyde (1.0 mmol) was selected as a model reaction (Scheme 1) and was examined under different conditions. Initially, we examined various catalysts such as NH_2SO_3H, $H_6P_2Mo_{18}O_{62}$, HNO_3, DABCO, Nano-Fe_3O_4 and also tested the un-catalyzed reaction (Table 1). Because of type of reaction that needs acidic or basic catalyst, or in another word needs a stimulus to begin a reaction and also base on previous work [82] we choice these catalysts to examine to in this reaction (Scheme 1). As shown in Table 1, among the catalysts tested, NH_2SO_3H(SA) gave the highest yield for the corresponding quinoline derivative (Table 1) [83-85].

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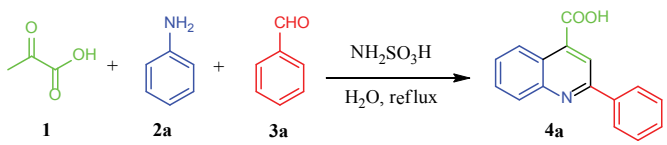


Scheme 1: Synthesis of **4a** as a model reaction.

Entry	Catalyst (mol %)	Time (hr)	Yield[b] (%)
1	NH_2SO_3H	3	90
2	$H_6P_2Mo_{18}O_{62}$	3	85
3	HNO_3	3	81
4	DABCO	4.5	59
5	Nano-Fe_3O_4	6	68
6	-	18	Trace

Table 1: Synthesis of 4a in presence of different catalysts in reflux condition. Synthesis of 4a in presence of different catalysts in reflux condition. a 1.2 mmol (1), 1.1 mmol (2a) and 1.0 mmol (3a) in presence of 3 mol% of catalyst and 5 mL of H_2O. [b]Refers to the isolated yield.

The other catalysts examined such as HNO_3 and $H_6P_2MO_{18}O_{62}$ were also effective but generally not as much (Table 1). To find a suitable solvent, the model reaction was carried out in different solvents (Table 2). The best result was achieved by conducting the reaction in the presence of 3 mol% of SA under reflux conditions in water (Table 2) [82,86]. It was also found out that the best result is achieved in the presence of 3 mol% of catalyst(SA) under reflux condition (Table 3). To establish, the substrate scope of this methodology, we reacted divergent benzaldehydes, and amines with pyruvic acid under the optimized reaction conditions to obtain the corresponding qiounoline-4-carboxylic acids in excellent yields (Scheme 2; 4a-i). All compounds were known and their structures were confirmed by comparison of physical and spectral data with those of already reported (Table 4). The results were listed in Table 4 [82]. A proposed mechanism for the SA-catalyzed formation of quinoline-4-carboxylic acid derivatives is proposed and shown in Scheme 3. The mechanism of this reaction using other catalysts was suggested and explained in recent years [90-93]. The proposed Sulfamic acid-catalyzed reaction involves the 1,2- addition of the aniline to aromatic aldehyde to form adducts **5**, which followed by elimination of H_2O to achieve intermediate **6**. The latter is subjected to Mannich reaction with pyruvic acid which followed by intermolecular cyclization, to afford the intermediate **8**, which in turn dehydrated and then dehydrated and oxidized to give the corresponding quinoline **4** [82] (Scheme 3). From the green chemistry points of view, experiments concerning the recycling and reuse of the catalyst (SA) was carried out. The insolubility of the catalyst SA in water made the catalyzed reaction, heterogeneous, thus the catalyst is separated by a simple filtration. Upon the completion of the reaction, monitored and observed with TLC, the catalyst SA was separated by filtration and reused. As shown in Figure 1, the catalyst could efficiently have recovered even after 4 cycles without suffering any significant drop in its catalytic activity or the yield of reaction (Figure 1) [82,83]. In summary, an extremely facile, high-yielding method for the preparation of quinoline-4-carboxylic acid derivatives under mild reaction conditions, *via* a one-pot MCR, in the presence of an efficient, highly effective, economically, and reusable solid acid heterogeneous catalyst in was developed. This catalyst could easily be separated from the reaction mixture with high yields and purity and can be directly reused after simple extraction. In addition, using water as green solvent and operational simplicity are the merits of this method. The procedure has many advantages such as short reaction time, the requirement of small amount of catalyst, mild acidity conditions, giving virtually quantitative yields and being performed under environmentally friendly conditions.

Experimental Section

Materials and equipment's

Chemicals and solvents were purchased from Merck-Aldrich and used directly with high-grade quality, without any purification. TLC

Entry	Solvent	Time (hr)	Temperature (°C)	Yield[b] (%)
1	H_2O	3	Reflux	90
2	CH_3CH_2OH	6.5	Reflux	80
3	CH_3CN	18	Reflux	Trace
4	-	26	100	69

Table 2: Synthesis of 4a in presence of different solvents. Synthesis of 4a in presence of different solvents. a 1.2 mmol (1), 1.1 mmol (2a) and 1.0 mmol (3a) in presence of 3 mol% of catalyst (Sulfamic acid) and 5 mL of solvent. [b]Refers to the isolated yield.

Entry (3212)	Catalyst mol %	Time (hr)	Temperature (°C)	Yield[b] (%)
1	2	4.5	Reflux	78
2	3	3	Reflux	90
3	4	3	Reflux	90
4	5	3	Reflux	90
5	2	5	100	62
6	3	5.5	100	50
7	2	8.5	120	43
8	4	9	130	75
9	3	4	70-80	71
10	3	5.5	90-100	77
11[c]	3	8	110-120	80

Table 3: Synthesis of 4a in presence of different amount of catalyst and temperature. Synthesis of 4a in presence of different amount of catalyst (Sulfamic acid) and temperature. a 1.2 mmol (1), 1.1 mmol (2a) and 1.0 mmol (3a). [b]Refers to the isolated yield. [c]In solvent free condition.

Entry	R^1	R^2	Product	Time (hr)	Yield[b] (%)	Mp (°C)/Lit. Mp [Ref]
1	H	H	4a	3	90	211-212/212-214 [82]
2	4-Me	H	4b	4	88	213-214/218-219 [83]
3	4-NO_2	H	4c	11	43	233-235/238-239 [84]
4	3-Cl	H	4d	4	80	256-259/256-260 [85]
5	H	4-OMe	4e	7	83	213-215/216-217 [86]
6	H	4-OH	4f	3	89	268-270/271-273 [87]
7	H	4-NO_2	4g	3	90	319-322/324 [88]
8	4-Me	4-OMe	4h	3.5	79	231-233/235-237 [89]
9	4-Me	4-NO_2	4i	5.5	91	263/265-266 [82]

Table 4: Synthesis of quinoline-4-carboxylic acid derivatives (4a-i) under optimized conditions Synthesis of quinoline-4-carboxylic acid derivatives (4a-i) under optimized conditions. a 1.2 mmol (1), 1.1 mmol (2) and 1.0 mmol (3) in presence of 3 mol% of catalyst (Sulfamic acid) and 5 mL H_2O at reflux condition. [b]Refers to the isolated yield.

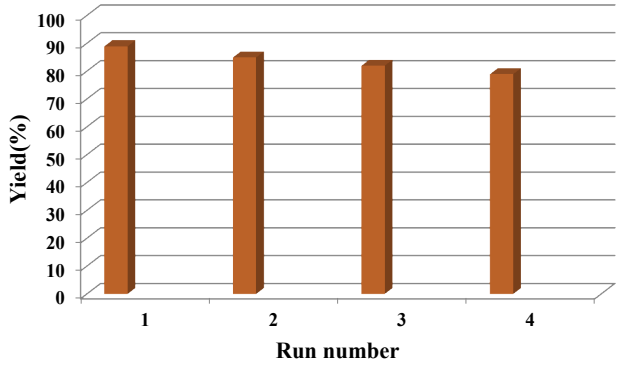
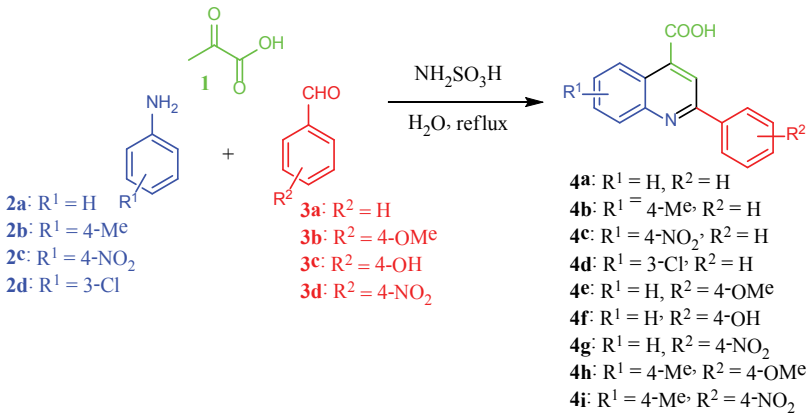
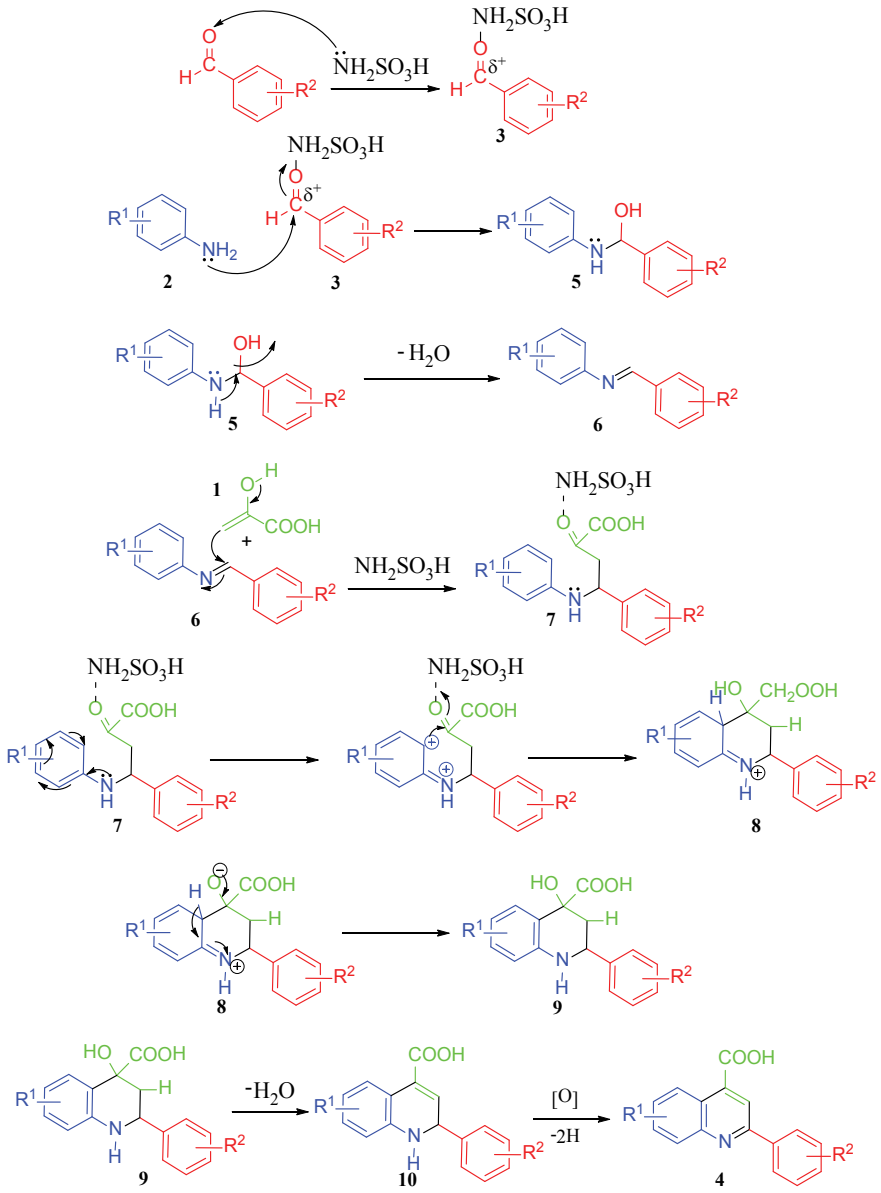


Figure 1: The recyclability of the SA in the preparation of 4a.



Scheme 2: Synthesis of quinoline-4-carboxylic acid derivatives.



Scheme 3: Proposed mechanism of the synthesis of **4**.

analyses were done using percolated TLC silica gel 60 F_{254} (Merck) plates. The ^{1}H NMR spectra were recorded by Bruker Ultrashield 500 MHz respectively advance instrument, with $CDCl_3$ used as solvent. Proton resonances are designated as singlet (s), doublet (d), triplet (t) and multiplet (m). FT-IR spectra were recorded using KBr disks on FTIR Bruker Tensor 27 instrument in the 500-4000 cm^{-1} region. The vibration transition frequencies are reported in wave numbers (cm^{-1}). Band intensities are assigned as weak (*w*), medium (*m*), and strong (*s*). Melting points were measured using a capillary tube method with a Barnstead Electrothermal 9200 apparatus. All products were known and identified by comparison of their physical and spectroscopic data with those of authentic compounds and found being identical. All yields refer to isolated products.

The synthesis of quinoline-4-carboxylic acid derivatives (4a-i)

General procedure: A mixture of pyruvic acid (1.2 mmol), amine (1.1 mmol), and benzaldehyde (1.0 mmol) in 5 ml of water was well stirred with NH_2SO_3H (3 mol%). This mixture was magnetically stirred under reflux for appropriate time according to Table 4. The progress of reaction was monitored by TLC (7:3, *n*-hexane/ethyl acetate). Upon completion of the reaction, the mixture was cooled to room temperature. After filtration, the catalyst which reminded in the aqueous phase can be recovered simply by removing the water through heating and the aqueous phase, and stored for use in subsequent run under the same conditions without any treatment.

The remaining solution is concentrated by increasing slightly CH_2Cl_2, and was magnetically stirred for 5 min. The precipitate was filtered to give quinoline-4-carboxylic acid as a crude. This crude was recrystallized with acetic acid to get pure product (Table 4; 4a-i) All the triazoles are known compounds, and their physical data were found to be identical with those of authentic samples [82-89].

Compound 4a: m.p.: 211-212°C [82]. IR (KBr): n=3429, 3335, 3042, 1679, 1590, 1487,1378 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): d=8.76 (d, 1H, J=8.5 Hz), 8.59 (s, 1H), 8.22 (d, 1H, J=8.5 Hz), 8.36 (d, 2H, J=7.4 Hz), 7.30 (t, 1H, J=7.5 Hz), 7.53 (t, 1H, J=7.5 Hz), 7.95 (m, 2H), 6.50 (m, 1H).

Compound 4b: m.p.: 213–214°C [87]. ^{1}H NMR (500 MHz, $CDCl_3$): d=7.50 (s, 1H), 8.55 (s, 1H), 8.20 (m, 2H), 8.10 (d, 1H, J=8.4 Hz), 7.36 (d, 1H, J=8.4 Hz), 7.70 (t, 2H, J=7.4 Hz), 7.22 (m, 1H), 2.62 (s, 3H).

Compound 4c: m.p.: 233–235°C [88]. ^{1}H NMR (500 MHz, $CDCl_3$): d=8.86 (d, 1H, J=8.9 Hz), 7.45 (m, 2H), 7.00–7.40 (m, 5H), 8.15 (m, 1H).

Compound 4d: m.p.: 256–259°C [89]. ^{1}H NMR (500 MHz, $CDCl_3$): d=8.52 (s, 1H), 8.20–8.39 (m, 2H), 7.49 (m, 5H), 7.89 (d, 1H, J=9.1 Hz).

Compound 4e: m.p.: 213–215°C [90]. ^{1}H NMR (500 MHz, $CDCl_3$): d=8.20 (s, 1H), 7.23 (d, 1H, J=8.9 Hz), 7.10 (d, 2H, J=8.0 Hz), 7.42 (t, 1H, J=7.0 Hz), 7.30 (d, 2H, J=8.9 Hz), 8.47 (d, 1H, J=8.0 Hz). 6.76 (t, 1H, J=7.1 Hz), 3.72 (s, 3H).

Compound 4f: m.p.: 268–270°C [91]. ^{1}H NMR (500 MHz, $CDCl_3$): d=8.23 (d, 1H, J=8.7 Hz), 7.51 (s, 1H), 8.22 (m, 3H), 7.50 (t, 1H, J=7.3 Hz), 8.38 (d, 2H, J=8.7 Hz), 6.62 (t, 1H, J=7.3 Hz).

Compound 4g: m.p.: 319-322°C [92].^{1}H NMR (500 MHz, $CDCl_3$): d=8.25 (d, 1H, J=8.0 Hz), 7.35 (s, 1H), 8.83 (m, 2H), 7.13 (d, 1H, J=8.1 Hz),7.78 (t, 1H, J=7.6 Hz), 7.56 (t, 1H, J=7.5 Hz), 7.00 (m, 2H).

Compound 4h: m.p.: 231–233°C [93]. ^{1}H NMR (500 MHz, $CDCl_3$): d=8.22 (s,1H), 8.41 (s, 1H), 8.29 (d, 2H, J=8.3 Hz), 7.16 (d, 1H, J=8.2 Hz), 7.85(d, 1H, J=8.3 Hz), 7.25 (d, 2H, J=8.4 Hz), 2.90 (s, 3H), 2.62 (s, 3H).

Compound 4i: m.p.: 263°C [82]. ^{1}H NMR (500 MHz, $CDCl_3$): d=8.95 (s,1H),7.52 (s, 1H), 8.47 (m, 4H), 8.49 (d, 1H, J=8.7 Hz), 7.23 (d, 1H, J=9.4 Hz),2.85 (s, 3H).

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