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Application of [Pyridine-1-SO_3H-2-COOH]Cl as an efficient catalyst for the preparation of hexahyroquinolines

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Abstract

Pyridinium-1-sulfonic acid-2-carboxylic acid chloride {[Pyridine-1-SO_3H-2-COOH]Cl} was synthesized and applied as a novel and efficient catalyst for the preparation of hexahydroquinolines by the one-pot multi-component condensation reaction of various aryl aldehydes with dimedone (5,5-dimethylcyclohexane-1,3-dione), *β*-ketoesters and ammonium acetate under mild and solvent-free conditions. Low cost, non toxic nature, simple work-up and excellent yields of products are the main advantages of this work.

Keywords: Pyridinium-1-sulfonic acid-2-carboxylic acid chloride; Hexahydroquinoline; multi-component condensation; β-ketoester; solvent-free.

Introduction

Multi-component reactions (MCRs), as a one-pot convergent strategy, have important role in combinatorial chemistry due to the ability to give desired compound with greater efficiency and atomic economy by the condensation of three or more compounds together in one step. Also, MCRs improve simplicity and synthetic efficiency on the organic synthesis [1-5].

Hexahydroquinoline (HHQs) derivatives are of importance as they have various pharmacological activities. This class of quinolines has diverse applications in biological and pharmacological chemistry, being applied as antiasthmatic, antibacterial antihypertensive, anti-inflammatory, antimalarial, and tyrosine kinase inhibiting compounds [6-11]. Some other protocols and catalysts have been reported for the preparation of HHQs [12-23]. The Hantzsch reaction is categorized as a one-pot, three-component process for the preparation of HHQs. Typically; it is accomplished using an aldehyde, *β*-dicarbonyls and ammonium acetate or ammonia at high temperature [24]. Several catalysts such as FeF_3 [19], $K_7[PW_{11}CoO_{40}]$ [25a], PPA-SiO_2 [25b], $HClO_4$-SiO_2 [25c], Fe_3O_4-SiO_2 [26], and SBISAC [27], have been introduced for the synthesis of HHQs.

The design and application of high efficiency catalysts in synthetic organic protocols such as metal-free organic molecules (organocatalysts) and organometallic catalysts have attracted a remarkable amount of interest from the scientific community in order to increase increasingly attractive methodologies for the synthesis of more

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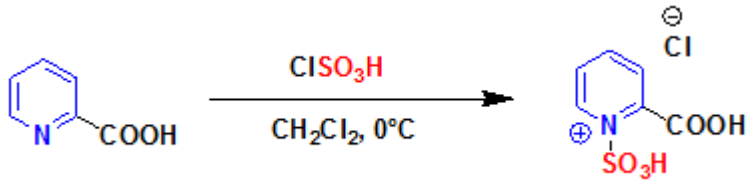
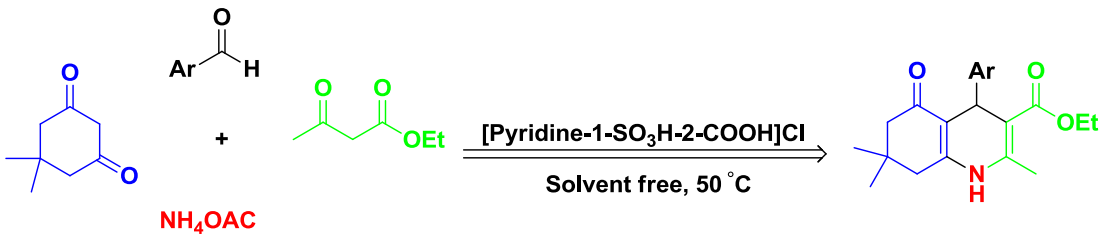
complex molecules [28]. Organocatalysts have a significant impact and direct benefit in the making of pharmaceutical intermediates when they are compared with (transition) metal catalysts.

Organocatalysts are commonly inexpensive, stable and readily accessible, show low toxicity and no sensitivity towards humidity or oxygen [29]. Another advantage of organocatalysts relates to their favorable surface to volume ratio which increases the contact between reactants and catalyst support and in turn increases the catalytic activity [30].

In this context, we have recently introduced a new pyridinium-1-sulfonic acid-2-carboxylic acid chloride {[Pyridine-1-SO_3H-2-COOH]Cl}, as an active and efficient organocatalyst, which was successfully used for the synthesis of different hexahydroquinoline derivatives exhibiting various significant properties (Schemes 1 and 2).



Scheme 1. The preparation of 1-Sulfopyridinium-2-carboxylic acid chloride



Scheme 2. The preparation of hexahydroquinolines

Experimental

General

All chemicals were purchased from Merck or Fluka Chemical Companies. The known products were identified by comparison of their melting points and spectral data with those reported in the literature. Progress of the reactions was monitored by TLC using silica gel SIL G/UV 254 plates.

General procedure for the preparation of [Pyridine-1-SO_3H-2-COOH]Cl

A round-bottomed flask was charged with 2-pyridinecarboxylic acid (0.615 g, 5 mmol) in CH_2Cl_2 (50 mL), and then chlorosulfonic acid (0.58 g, 5 mmol) was added dropwise over a period of 5 min at 0 °C. After the addition was completed, the reaction mixture was stirred for 20 minutes, and the CH_2Cl_2 was decanted. The residue was washed with dry CH_2Cl_2 (3×50 mL) and dried under vacuum to give pyridinium-1-sulfonic acid-2-carboxylic acid chloride {[Pyridine-1-SO_3H-2-COOH]Cl} as a white precipitate in 95% yield.

General procedure for the synthesis of hexahydroquinolines

A mixture of aldehyde (1 mmol), dimedone (1 mmol), ethyl acetoacetate (1 mmol) and ammonium acetate (1.2

mmol) and {[Pyridine-1-SO_3H-2-COOH]Cl (0.167 g, 7 mol%) in a 25 mL round-bottomed flask, was stirred in an oil-bath (50 °C). After completion of the reaction, as monitored by TLC, the reaction mixture was cooled to room temperature. Afterward, H_2O was added to the reaction mixture, stirred for 5 min [the catalyst is soluble in H_2O; however, the product is not soluble in H_2O]. The mixture of reaction isolated, and the crude product was purified by recrystallization from ethanol (95%).

Ethyl4-(2,5-dimethoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate
White solid; IR (KBr): 3299, 3080, 2961, 2835, 1696, 1647, 1603, 1380, 1214cm^{-1}; ^{1}H NMR: (400 MHz, DMSO-*d*6) δ = 0.81 (s, 3H, CH_3), 1.20 (s, 3H, CH_3), 1.18 (t, *J*=8 Hz, 3H, CH_3), 1.98 (d, *J* =1.6 Hz, 1H, CH), 1.98 (d, *J*=1.6 Hz, 1H, CH), 2.41 (s, 3H, CH_3), 2.52 (d, *J* =1.6 Hz, 1H, CH), 2.52 (d, *J*=1.6 Hz, 1H, CH), 3.65 (d, *J*=7.6 Hz, 6H, $2CH_3$), 3.93 (q, *J*=3.2 Hz, 2H, CH_2), 5.01 (s, 1H, CH), 6.63 (d, *J*=3.2 Hz, 1H, ArH), 6.67 (q, *J* =2.8 Hz, 1H , ArH), 6.77 (d, *J*=8.8 Hz, 1H , ArH), 8.97 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-*d*6) δ 14.6, 18.5, 26.7, 29.8, 32.5, 33.6, 42.2, 48.0, 50.9, 55.6, 56.4, 59.3, 103.4, 109.0, 111.3, 112.5, 117.3, 136.6, 150.5, 152.1, 153.0, 167.8, 194.3.

Ethyl2,7,7-trimethyl-5-oxo-4-(thiophen-2-yl)-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate
White solid; IR (KBr): 3287, 3219, 2972, 1696, 1643, 1384, 1283, 1210 cm^{-1}; ^{1}H NMR: (400 MHz, DMSO-*d*6) δ = 0.96 (s, 3H, CH*3*), 1.04 (s, 3H, CH_3), 1.20 (t, *J*=2.8 Hz, 3H, CH_3), 2.08 (d, *J* =16.8 Hz, 1H, CH), 2.23 (d, *J*=16 Hz, 1H, CH), 2.28 (d, *J*=6.2 Hz, 1H, CH), 2.34 (s, 3H, CH_3), 2.44 (d, *J*=17.2 Hz, 1H, CH), 4.10 (q, *J*=6.4 Hz, 2H, CH_2), 5.19 (s, 1H, CH), 6.67 (dd, *J*=1.2 Hz, 0.8 Hz, 1H, ArH), 6.84-6.67 (m, 1H, ArH), 7.19 (dd, *J* =3.6, 1.2, 1H , ArH), 8.974 (s, 1H, NH); ^{13}C NMR (100MHz, DMSO-*d*6) δ 14.7, 18.7, 27.0, 29.6, 31.0, 32.6, 50.6, 59.7, 103.5, 109.9, 123.0, 123.7, 126.8, 146.0, 150.3, 152.0, 167.1, 194.7.

Ethyl4-(2,4-dimethoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate
White solid; IR (KBr): 3292, 3243, 3083, 2953, 1695, 1448, 1496, 1380, 1215cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ = 0.95 (s, 3H, CH_3), 1.02 (s, 3H, CH_3), 1.22 (t, *J*=7.2 Hz, 3H, CH_3), 2.13 (d, *J* =4 Hz, 1H, CH), 2.18 (d, *J*=9.2 Hz, 1H, CH), 2.22 (d, *J*=12.8 Hz, 1H, CH), 2.29 (s, 3H , CH_3), 2.32 (d, J=7.2 Hz, 1H, CH), 3.77 (d, J=9.2 Hz, 6H, $2CH_3$), 4.06 (q, *J*=3.6 Hz, 2H, CH_2), 5.18 (s, 1H, CH), 6.39-6.36 (m, 2H, ArH), 7.22 (d, *J* =4 Hz, 1H , ArH), 7.29 (s, 1H, NH); 13C NMR (100MHz, $CDCl_3$) δ 14.2, 19.0, 26.7, 29.6, 32.4, 33.0, 40.7, 50.8, 55.1, 55.2, 59.5, 98.3, 103.8, 104.9, 110.4, 127.5, 131.5, 143.5, 149.8, 158.4, 159.0, 168.1, 195.6.

Ethyl4-(4-(dimethylamino)phenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate
Yellow solid; IR (KBr): 3282, 3080, 3209, 2801, 1702, 1684, 1518, 1489, 1345, 776 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ = 0.970 (s, 3H, CH_3), 1.097 (s, 3H, CH_3), 1.265 (t, *J* = 4 Hz, 3H, CH_3), 2.195 (d, *J* = 6.8 Hz, 1H, CH_2), 2.27 (d, *J* = 3.2 Hz, 1H, CH), 2.37 (s, 3H, CH_3), 2.89 (s, 6H, $2CH_3$), 2.99 (s, 2H, CH_2), 4.09 (q, *J* = 7.2 Hz, 2H, CH_2), 4.98 (s, 1H, CH), 6.39 (s, 1H, NH), 6.64 (d, *J* = 8.8 Hz, 2H , ArH), 7.19 (dd, *J* = 4.8 Hz, 2 Hz, 1H , ArH), 7.29 (s, 1H, ArH); ^{13}C NMR (100MHz, $CDCl_3$) δ 14.3, 19.1, 27.2, 29.6, 32.5, 35.4, 40.4, 40.7, 50.9, 59.7, 106.2, 111.7, 112.3, 128.6, 136.1, 143.7, 148.8, 149.9, 167.9, 196.2.

Results and discussion

At first, 2-pyridinecarboxylic acid in CH_2Cl_2 (50 mL) was reacted with chlorosulfonic acid at 0 °C. Then, the reaction mixture was stirred for 20 minutes, and The residue was washed with dry CH_2Cl_2 and dried under vacuum to prepare pyridinium-1-sulfonic acid-2-carboxylic acid chloride {[Pyridine-1-SO_3H-2-COOH]Cl} as a white precipitate.

The structure of pyridinium-1-sulfonic acid-2-carboxylic acid chloride {[Pyridine-1-SO_3H-2-COOH]Cl}was identified by IR, ^{1}HNMR, ^{13}CNMR and mass spectra (Schemes **S1-S4**).

In the next step, catalytic activity of [Pyridine-1-SO_3H-2-COOH]Cl was tested on the preparation of hexahydroquinolines. To optimize the reaction conditions, the condensation of dimedone (1 mmol), 4-nitrobenzaldehyde (1 mmol), ethyl acetoacetate (1 mmol) and ammonium acetate (1.2 mmol), as a model reaction, was examined in the presence of different quantities of the [Pyridine-1-SO_3H-2-COOH]Cl, at range of 25–100 °C under solvent-free conditions. The respective results are summarized in Table 1. The reaction was examined in the presence of 3, 5, 7 and 10 mol% of [Pyridine-1-SO_3H-2-COOH]Cl. The best results regarding reaction time and yield was obtained using 7 mol% of the catalyst (Table 1, Entry 2). Increasing the amount of catalyst did not improve the reaction time and yield. To investigate the effect of temperature, the model reaction was carried out in the range of 25–100 °C. It was indicated that 50 °C was the suitable temperature to carry out this reaction.

Table 1. Effect of the catalyst amount and temperature on the reaction between dimedone, 4-nitrobenzaldehyde, ethyl acetoacetate and ammonium acetate

Entry	Catalyst	Catalyst amount (mol%)	Temp.(°C)	Time (min)	Yield[a] (%)
1	[Pyridine-1-SO_3H-2-COOH]Cl	7	25	20	70
2	[Pyridine-1-SO_3H-2-COOH]Cl	7	50	5	93
3	[Pyridine-1-SO_3H-2-COOH]Cl	7	70	5	93
4	[Pyridine-1-SO_3H-2-COOH]Cl	7	100	5	93
5	[Pyridine-1-SO_3H-2-COOH]Cl	3	50	25	75
6	[Pyridine-1-SO_3H-2-COOH]Cl	5	50	10	90
7	[Pyridine-1-SO_3H-2-COOH]Cl	10	50	5	93

[a]Isolated yield

To investigate the efficacy of solvent, we tested the model reaction in different solvents, including $CHCl_3$, H_2O, CH_2Cl_2, EtOAC, EtOH, acetone and n-hexane using 7 mol% of the catalyst under refluxing conditions. The results of these experiments showed that the use of a solvent was reduced the yield of the desired product in all cases in comparison with the obtained yield under solvent-free conditions (Table 2, Entries 1–7).

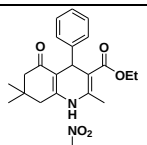
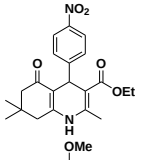
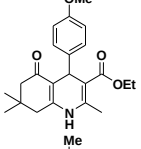
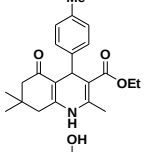
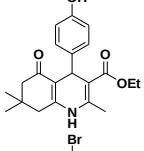
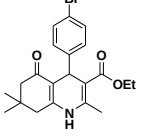
Table 2. Effect of various solvents on the reaction of dimedone (1 mmol), 4-nitrobenzaldehyde (1 mmol), ethyl acetoacetate (1 mmol) and ammonium acetate (1.2 mmol), in the persence of [Pyridine-1-SO_3H-2-COOH]Cl (0.0167 g, 7 mol %)

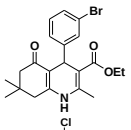
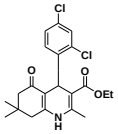
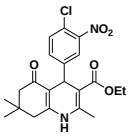
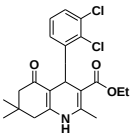
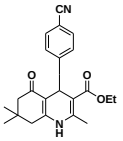
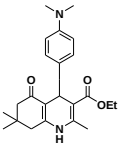
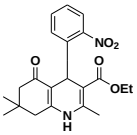
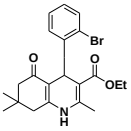
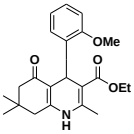
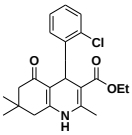
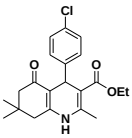
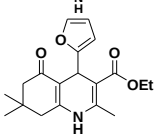
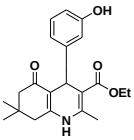
Entry[a]	Solvent	Temp. (°C)	Time (min)	Yield[b] (%)
1	$CHCl_3$	50	30	66
2	EtOAc	50	15	78
3	CH_2Cl_2	Reflux	35	70
4	H_2O	50	-	-
5	Acetone	Reflux	20	70
6	n-hexane	50	30	60
7[c]	$CHCl_3$	50	5	93

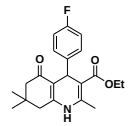
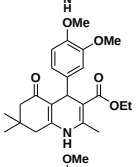
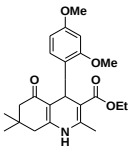
[a]All reactions were carried out at 50 ºC except entries 3 and 6, which was proceeded at reflux condition. [b]Isolated yield. [c]The reaction was proceeded in the absence of solvent.

After the optimization of reaction conditions, the synthesis of various hexahydroquinolines was tested to investigate the efficacy and the scope of the presented method. The obtained results are given in Table 3. Various aromatic aldehydes containing electron-releasing substituents, electron-withdrawing substituents and halogens on their aromatic ring were successfully reacted with dimedone and ethyl acetoacetate to give high to excellent yields of products in short reaction times under solvent-free conditions. Therefore, [Pyridine-1-SO_3H-2-COOH]Cl, was a highly efficient and general catalyst for the preparation of HHQs.

Table 3. The solvent-free synthesis of HHQs from dimedone, arylaldehydes, *β*-ketoesters and ammonium acetate catalyzed by [Pyridine-1-SO_3H-2-COOH]Cl at 50 °C

Entry	Product	Time (min)	Yield[a] (%)	M.p. °C (Lit.)
1		7	81	204-205 (204-205) [26]
2		5	92	245-258 (245-247) [26]
3		5	90	255-259 (257-259) [26]
4		6	85	262-263 (262-263) [26]
5		7	85	238-241 (238-241) [26]
6		5	92	249-253 (250-252) [26]

7		6	75	227-230 (229–230) [26]
8		5	89	244-245 (243-245) [22]
9		7	73	214-217 (214–216) [26]
10		5	89	229-234 (229-234) [17]
11		10	85	239-240 (238-240) [26]
12		7	95	205-207 (205-207) [26]
13		5	92	255-256 (257-259) [22]
14		5	92	208-209 (208–209) [26]
15		5	95	247-251 (245-256) [23]
16		12	78	248-249 (248–249) [26]
17		10	80	216-217 (211-213) [22]
18		5	89	244-245 (243-245) [32]
19		7	73	214-216 (220) [32]

20		5	89	229-234
21		10	70	241-242
22		10	85	239-240 (246) [32]

[a]Isolated yield

To compare the efficiency of [Pyridine-1-SO_3H-2-COOH]Cl with the previously reported catalysts for the preparation of hexahydroquinolines, we have summarized the results of [Pyridine-1-SO_3H-2-COOH]Cl to perform the condensation reaction of dimedone, 4-nitrobenzaldehyde, ethyl acetoacetate and ammonium acetate in comparison with some other catalysts on this reaction in Table 4. As Table 4 indicates that [Pyridine-1-SO_3H-2-COOH]Cl has remarkably improved the preparation of hexahydroquinolines. The reaction time was shorter, and the yield of product was higher using [Pyridine-1-SO_3H-2-COOH]Cl.

Table 4. Comparison the efficiency of [Pyridine-1-SO_3H-2-COOH]Cl with various reported catalysts on the model reaction

Entry	catalyst	Catalyst loading	Time	Yield (%)[Ref]
1	Silica gel/$NaHSO_4$	5 mol%	6 h	85 [31]
2	HClO4-SiO_2/80 °C	0.05 g	20 min	95 [31]
3	CAN	5 mol%	1 h	92 [31]
4	L-Proline	10 mol%	0.5 h	95 [31]
5	PSA	4.5 mol%	15 min	98 [31]
6	Fe_3O_4-SiO_2	5 mol%	5 min	92 [31]
7	SBISAC	0.005 g	6 min	93 [31]
8	[Pyridine-1-SO_3H-2-COOH]Cl	7 mol%	5 min	93

The proposed mechanism shows the preparation of the HHQ_S (Scheme 3) which is supported by the previous literature [13,15,17,22,23,26]. At first, dimedone is converted to its enol form using [Pyridine-1-SO_3H-2-COOH]Cl as a Brønsted acid and reacted to activated aldehyde (by [Pyridine-1-SO_3H-2-COOH]Cl) to generate intermediate **I**. Also, by the reaction of activated *β*-ketoester (by the catalyst) and ammonia (resulted from ammonium acetate) enamine **II** is prepared. Then, the intermediate **I** is reacted with enamine **II** to prepare intermediate **III**. **III** is converted to **IV** by tautomerization, and

intermediate **IV** forms **V** by intramolecular nucleophilic attack of the NH_2 group to the activated carbonyl group and then removing one molecule H_2O. Afterward, the expected hexahydroquinonine prepared by tautomerization of **V**.

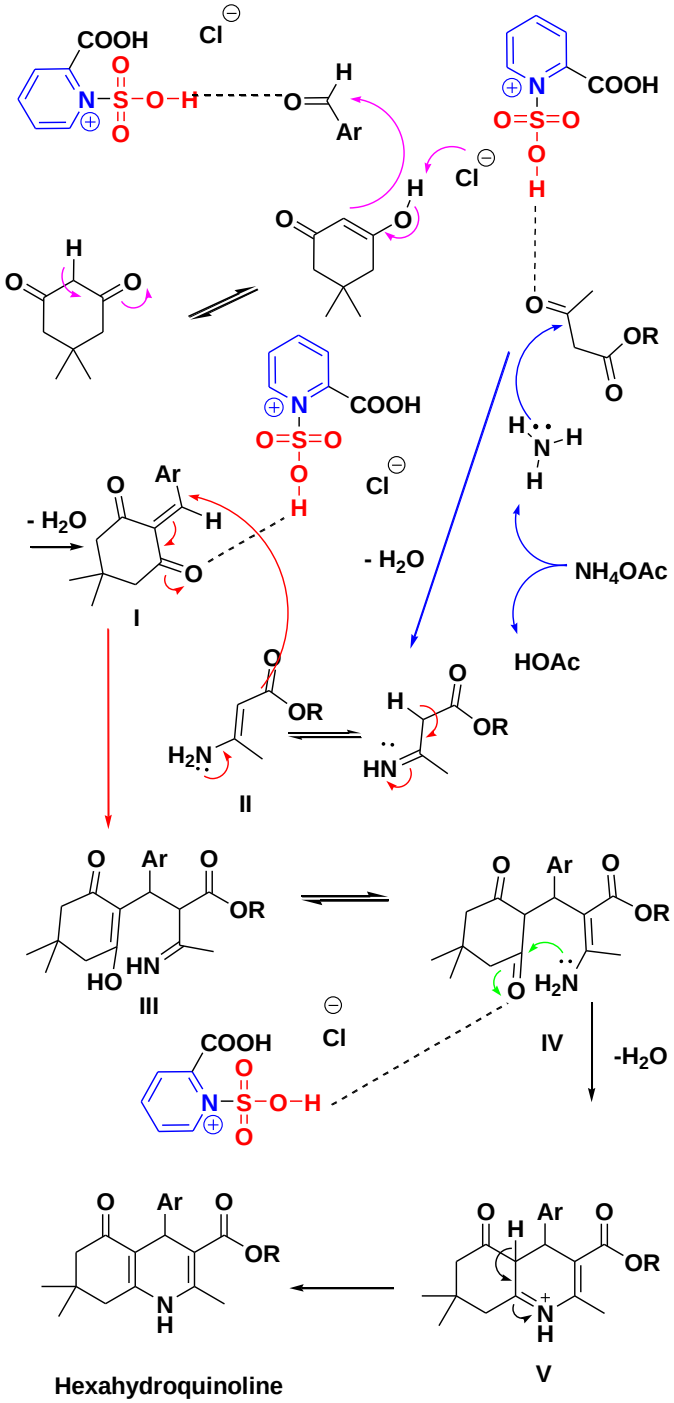


Table 3. Proposed mechanism for the synthesis of hexahydroquinonines

Conclusion

In summary, we have introduced a simple and efficient method for the preparation of hexahydroquinolines using [Pyridine-1-SO_3H-2-COOH]Cl as an inexpensive and available catalyst. Mild reaction condition, simple procedure, cleaner reactions, short reaction times and high yields of

products are some important advantages of the presented work.

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Supporting information
Supplemental data for this article can be accessed on the publisher's website.

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