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Highly efficient Brønsted acid and Lewis acid catalysis systems for the Friedländer Quinoline synthesis

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ABSTRACT

The efficient and green Brønsted acid or Lewis acid catalysis systems for the Friedländer synthesis of 2,3,4-trisubstituted quinolines from the condensation of 2-aminoarylketones and β -ketoesters/ketones had been developed. The results confirmed that 4-toluenesulfonic acid, magnesium chloride, and cupric nitrate were the desired catalyst independently. This protocol had the advantages of mild conditions, operational simplicity, and excellent yields.

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Brønsted acid; catalysis; Friedländer; Lewis acid; Quinoline

GRAPHICAL ABSTRACT



Quinolines are one of the most privileged azaheterocyclic scaffolds, which are commonly found in many pharmaceuticals^[1] and natural products.^[2] Besides, they are wildly applied to the preparation of metal complexes as ligand.^[3] Thus, the exploration of synthetic methods of quinolines is a topic area for organic synthesis chemists.^[4] In the past decades, several classical approaches had been developed for the construction of quinoline derivatives, including the Skraup–Doebnervon Miller,^[5] Pfitzinger,^[6] Combes reactions,^[7] and Friedländer quinoline synthesis.^[8] Among these methods, the Friedländer reaction is one of the simplest protocols, which involves condensation of 2-aminoaryl ketones and β -ketoesters/ketones possessing a reactive α -methylene group.

Recently, many novel Brønsted acid or Lewis acid catalysis systems have been developed. For example, Heydari's group^[9] developed the one-pot domino approach to realize Friedländer quinoline synthesis in aqueous medium, using SO_3H -functionalized ionic liquid as a water-tolerant acidic catalyst. In 2012, Rao's group^[10] reported (bromodimethyl)sulfonium bromide-catalyzed Friedländer quinoline synthesis in

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Supplemental data (Full experimental detail, ¹H and ¹³C NMR spectra) can be accessed on the publisher's website. © 2018 Taylor & Francis

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solvent-free conditions. In 2013, Pérez-Mayoral et al.^[11] developed a series of acidic activated carbon material-catalyzed Friedländer reactions and the results indicated that the most acidic microporous carbon materials were efficient catalysts and a cheap alternative for the synthesis of quinolines through Friedländer condensation. In 2014, the ball milling technique was used for Friedländer reactions in the presence of 4-toluenesulfonic acid under solvent-free conditions.^[12] In 2015, Esmaeilpour and Javidi^[13] developed green and reusable $Fe_3O_4@SiO_2$ -imid-PMAh and $Fe_3O_4@SiO_2$ -imid-PMAb nanoparticle-catalyzed Friedländer reactions of 2-aminobenzophenones and ethylacetoacetate or ketones.

In addition, several modified Friedländer reactions had been developed, involving the reactions of aromatic 2-aminosubstituted carbonyl compounds with various other substrates, such as alkynes,^[14] alkenes,^[15] alcohols,^[16] 2-aminoaryl methanols,^[17] 2-iodoanilines,^[18] and 2-nitroaryl aldehydes.^[19] In 2016, Ying et al.^[20] developed heterogeneous Ag-Pd/C alloy nanoparticle-catalyzed modified Friedländer reactions, with ketones and primary alcohols as substrates, to give polysubstituted quinolines in moderate to good yields. In the same year, Jiang's group^[21] reported the palladium-catalyzed aerobic oxidative approach to afford functionalized 2-substituted quinolines in moderate to good yields from readily available allylbenzenes with aniline. Subsequently, Kirchner et al.^[22] reported hydride Mn(I) PNP complex-catalyzed Friedländer-type quinoline synthesis with 2-aminobenzyl alcohols and secondary alcohols as substrates. Most recently, Popowycz et al.^[23] developed a Friedländer-type quinoline synthesis method starting from substituted anthranilonitriles. And 4-aminoquinolines were prepared in the presence of superacidic trifluoromethanesulfonic acid. The methods are effective, but there still are many drawbacks. They require the use of expensive reagents or metal catalysts, harmful organic solvents, or large excess amount of metal salts, which will limit their usefulness in large-scale production.

4-Toluenesulfonic acid, magnesium salts, and copper salts are a kind of most useful reagents in organic synthesis and can be used as cheap Brønsted acid or Lewis acid catalysts. To the best of our knowledge, the magnesium chloride and cupric nitrate-catalyzed Friedländer quinoline synthesis have not been reported previously. Herein, we reported three efficient catalysis systems for the Friedländer quinoline synthesis, using 4-toluenesulfonic acid (TsOH · H₂O), magnesium chloride (MgCl₂ · 6H₂O), and cupric nitrate (Cu(NO₃)₂ · 3H₂O) as the catalyst independently (Scheme 1).

In the course of our continuous research on copper-catalyzed enamination of ketones for the synthesis of enaminones,^[24] 1-(2,4-dimethylquinolin-3-yl)ethanone (**3a**) was prepared unexpectedly when 1-(2-aminophenyl)ethanone (**1a**) and pentane-2,4-dione (**2a**) were chosen as starting materials. Then, the initial experiment began with copper(I) chloride (CuCl) as catalyst in ethanol at 80 °C. The product **3a** was isolated with 57% yield



Scheme 1. Brønsted acid- and Lewis acid-catalyzed Friedländer quinoline synthesis.

	CH ₃ + 0 0 NH ₂ + H ₃ C CH ₃	Cat. (x mol%) Solvent, T °C	
	1a 2a	3а	
Entry	Cat.(x)	Solvent (T)	Yield (%) ^b
1	CuCl (10)	EtOH (80)	57
2	CuBr (10)	EtOH (80)	63
3	Cul (10)	EtOH (80)	16
4	$Cu(OAc)_2 \cdot H_2O$ (10)	EtOH (80)	Trace
5	$Cu(acac)_2$ (10)	EtOH (80)	Trace
6	$Cu(NO_3)_2 \cdot 3H_2O$ (10)	EtOH (80)	>99
7	$TsOH \cdot H_2O$ (10)	EtOH (80)	83
8	$TsOH \cdot H_2O$ (20)	EtOH (80)	>99
9	$TsOH \cdot H_2O$ (20)	MeOH (80)	>99
10	$TsOH \cdot H_2O$ (20)	Acetonitrile (80)	65
11	$TsOH \cdot H_2O$ (20)	1,4-dioxane (80)	56
12	TsOH \cdot H ₂ O (20)	THF (80)	Trace
13	TsOH \cdot H ₂ O (20)	Toluene (80)	41
14	TsOH \cdot H ₂ O (20)	EtOH (60)	81
15 ^c	TsOH \cdot H ₂ O (20)	EtOH (80)	70
16 ^d	TsOH \cdot H ₂ O (20)	EtOH (80)	78
17	LiCl (40)	EtOH (80)	71
18	LiCl (100)	EtOH (80)	81
19	NaCI (100)	EtOH (80)	19
20	$FeCl_3 \cdot 6H_2O$ (10)	EtOH (80)	86
21	$CoCl_3 \cdot 6H_2O$ (10)	EtOH (80)	97
22	$Zn(OAc)_2$ (10)	EtOH (80)	nr
23	$MgCl_2 \cdot 6H_2O$ (10)	EtOH (80)	>99
24	MgO (10)	EtOH (80)	Trace
25	MgSO ₄ (10)	EtOH (80)	12

Table 1. Optimization conditions for the Friedländer quinoline synthesis.^a

^aUnless otherwise stated, all reactions are performed with 1a (68 mg, 0.5 mmol), 2a (100 mg, 1.0 mmol), catalyst, and solvent (3.0 mL) in air, 12 h.

^blsolated yields are provided.

^c2a (60 mg, 0.6 mmol) was added.

^d2a (75 mg, 0.75 mmol) was added.

THF, tetrahydrofuran.

(Table 1, entry 1). This result encouraged us to expand catalysis system of Friedländer reactions. Then the catalysts, solvents, and temperature were evaluated to improve the yields of the reaction, respectively.

First, the other copper salts, CuBr (10 mol%), CuI (10 mol%), Cu(OAc)₂ · H₂O (10 mol%), Cu(acac)₂ (10 mol%), and Cu(NO₃)₂ · 3H₂O (10 mol%) were tested as the catalyst (entries 2–6) in EtOH at 80 °C and >99% yield was obtained when Cu(NO₃)₂ · 3H₂O (10 mol%) was chosen as catalyst (entry 6). The results indicated that the catalyst with stronger Lewis acidic properties favored to activate the ketones in the condensation. Then, 4-toluenesulfonic acid (TsOH · H₂O, 10 mol%) (entry 7) was tested as a Brønsted acidic catalyst and 83% yield was obtained. The yield was increased to >99% when 20 mol% TsOH · H₂O was added (entry 8).

To evaluate the effect of solvent, methanol (MeOH, >99%, entry 9), acetonitrile (65%, entry 10), 1,4-dioxane (56%, entry 11), tetrahydrofuran (trace, entry 12), and toluene (41%, entry 13) were tested as solvent, respectively. The results showed that both EtOH and MeOH were the best choice. Due to the convenient operation of experiment, EtOH was chosen as solvent in the following reaction optimization process. Subsequently, the temperature and amount of substrate 2a were tested (entries 14–16). The results

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confirmed that the best temperature was 80 °C and the best amount of 2a was 2.0 equivalents.

To investigate whether the other metal salts with Lewis acid could be used as catalyst in the Friedländer quinoline synthesis, lithium chloride (LiCl, 71% yield with 40 mol% loading and 81% yield with 100 mol% loading, entries 17–18), NaCl (100 mol%, 19%, entry 19), FeCl₃ · 6H₂O (10 mol%, 86%, entry 20), CoCl₃ · 6H₂O (10 mol%, 97%, entry 21), Zn(OAc)₂ (10 mol%, no product was detected, entry 22), MgCl₂ · 6H₂O (10 mol%, >99%, entry 23), MgO (10 mol%, trace, entry 24), and MgSO₄ (10 mol%, 12%, entry 25) were evaluated independently and the MgCl₂ · 6H₂O showed the best result with >99% yield. In conclusion, cupric nitrate (Cu(NO₃)₂ · 3H₂O, 10 mol%), 4-toluenesulfonic acid (TsOH · H₂O, 20 mol%), and magnesium chloride (MgCl₂ · 6H₂O, 10 mol%) were all the best catalyst for the Friedländer quinoline synthesis.

Thus, the standard conditions were established as follows: 4-toluenesulfonic acid (TsOH \cdot H₂O, 20 mol%), magnesium chloride (MgCl₂ \cdot 6H₂O, 10 mol%), or cupric nitrate (Cu(NO₃)₂ \cdot 3H₂O, 10 mol%) were used as catalysts in EtOH at 80 °C. Based on the optimized conditions, the substrate scope of the Friedländer quinoline synthesis was tested independently. The results are shown in Table 2.

Under the optimal conditions, a variety of 2-aminoarylketones and β -ketoesters/ketones were subjected to 4-toluenesulfonic acid (TsOH · H₂O, 20 mol%), magnesium chloride (MgCl₂ · 6H₂O, 10 mol%), and cupric nitrate (Cu(NO₃)₂ · 3H₂O, 10 mol%)-catalyzed Friedländer reaction, respectively, as shown in Table 2. For the condensation of substrates **1a-1e** and **1g-1i** (Table 2, entries 1–5, 7–9) with different substituents reacted with pentane-2,4-dione (**2a**) under the optimal reaction conditions **A**, **B**, and **C**, good to excellent yields (64– >99% yields) of **3a-3e** and **3g-3i** were achieved, respectively. The reaction was inhibited when substrate **1f** was applied to the synthesis of quinoline under optimal reaction conditions (entry 6). The reactivity of **1f** may be weakened by the steric hindrance of chlorogroup of 2-chlorophenyl and the stronger electron-withdrawing property of substituent –NO₂. It is worth to note that the catalysis system also can be applied to the substrate (2-aminophenyl)methanol **1j**, but only with 37–64% yield under the above three catalysis systems, respectively (entry 10).

Then, heptane-3,5-dione (**2b**, entry 11), 1-phenylbutane-1,3-dione (**2c**, entry 12), ethyl 3-oxobutanoate (**2d**, entry 13), and *iso*-propyl 3-oxobutanoate (**2e**, entry 14) were chosen as the substrate and reacted with **1a**, respectively. About 94%- >99% yields of target products were isolated. And when **2c** reacted with **1a**, only 19-74% yields of **3n** were isolated. The reason was speculated that the substrate **2c** with phenyl substituent increased the steric hindrance.

To test the scale-up procedure of Brønsted acid- and Lewis acid-catalyzed Friedländer quinoline synthesis, 1-(2-aminophenyl)ethanone **1a** (5.0 g) was input into the reaction under the optimized reaction conditions. And 1-(2,4-dimethylquinolin-3-yl)ethanone **3a** was attained with 94.6, 97.3, and 91.9% yields in the optimized catalysis systems **A**, **B**, and **C**, respectively. (Table 3). And the yields have decreased distinctly in the conditions **A** and **C** due to the raw material **1a** does not react completely (entries 1 and 3). The result indicated that magnesium chloride (MgCl₂ · 6H₂O) catalyst may be more appropriate for the scale-up procedure.

In summary, 4-toluenesulfonic acid (TsOH \cdot H₂O), magnesium chloride (MgCl₂ \cdot 6H₂O), and cupric nitrate (Cu(NO₃)₂ \cdot 3H₂O)-catalyzed Friedländer reaction of

		TsOH•H ₂ O (20 mol%)		
		or MaCl ₂ •6H ₂ O (10 mol%)		
	Q	or	R ¹ Q	
	R1 .	$\begin{array}{c} 0 O \\ \downarrow \downarrow \downarrow \downarrow \underbrace{Cu(NO_3)_2 \cdot 3H_2O(10 \text{ mol}\%)}_{\bullet} \end{array}$	R^4	
	R-T	R ^{3 /} R ⁴ EtOH, 80 °C		
	1	2	3	
Entry	Substrate 1	Product	Conditions	Yield (%) ^b
1	0	CH o	A	> 00
I		I CH3	R	>99
	NH.	CH3	C C	>99
	1a	3a	L.	///
2	0	Ph O	Α	>99
		CT CH3	В	>99
	NH ₂	N ¹ CH ₃	C	96
2	1 b	30		
3		Ä	A	>99
		\bigvee	B	93
		СН3	L L	92
	It	N CH3		
		3c		
4			Α	92
	< T T ^{℃H} ³	(TTT CH3	В	>99
	0 NH2	O CH3	C	90
F	ld	3d		07
2	O ₂ N		A	>00
		o,n. a I I	B	>99 01
	1e	III CH,	L L	71
		3e		
6		\sim	Α	Trace
			В	Trace
		O ₂ N CH _a	C	nr
	1f			
		3f		
7			Α	75
			В	86
	NH2	CI CH3	C	64
		N CH3		
		3g		
8	O F	Ň	Α	87
		F O	В	>99
		CI CH	C	93
	1h			
		3h		
9	O F		Α	>99
	[®] √ √ √	F O	В	>99
	NH2	Br	C	>99
	1i	LII ^{CH3}		
		СH ₃ З:		
10	СССОН	3 1	Α	37
	L NHa	сна	В	64
	1j	N CH3	C	44
	U	3i		
11	0	CH3 O	Α	98
	CH3		В	>99
	NH ₂	N Et	C	94
	1a	3k		

 Table 2.
 The test of substrate scope for Friedländer quinoline synthesis^a.

(Continued)

Entry	Substrate 1	Product	Conditions	Yield (%) ^b
12	0	сн ₃ о I II	Α	33
	СН3	Ph	В	74
	NH2	N CH3	C	19
	1a	31		
13	0	сн, о	Α	>99
	СН3	OEt	В	>99
	NH2	N CH3	C	96
	1a	3m		
14	0		Α	>99
	СН3	O'Pr	В	>99
	NH ₂	CH ₃	C	>99
	1a	3n		

Table 2.Continued.

^{*a*}Reaction conditions **A**:1 (0.5 mmol), **2** (1.0 mmol), TsOH · H₂O (19.0 mg, 0.1 mmol), and EtOH (3.0 mL) in air, 80 °C, 12 h; reaction conditions **B**: 1 (0.5 mmol), **2** (1.0 mmol), MgCl₂ · 6H₂O (10.2 mg, 0.05 mmol), and EtOH (3.0 mL) in air, 80 °C, 12 h; reaction conditions **C**: 1 (0.5 mmol), **2** (1.0 mmol), Cu(NO₃)₂ · 3H₂O (12.1 mg, 0.05 mmol), and EtOH (3.0 mL) in air, 80 °C, 12 h. ^{*b*}Isolated yield.

2-aminoaryl ketones and β -ketoesters/ketones had been successfully developed under green, efficient, and mild reaction conditions independently. The process afforded polysubstituted quinolines with moderate to excellent yields. And these catalysis systems will provide a powerful means to develop new applications of Brønsted acid or Lewis acid catalysts in the activation of carbonyl compounds and expand the synthesis approach for the preparation of heterocyclic compounds.

Experimental section

General methods: All commercially available reagents were used without further purification. Column chromatography was performed on silica gel (200–400 mesh). The chemical shifts (δ) of the ¹H NMR (400 MHz) signals are reported in ppm relative to tetramethylsilane (TMS) and using the residual solvent resonance as the internal standard. Data are reported in the following order: chemical shift, multiplicity [s (singlet), d (doublet), dd (doublet of doublets), t (triplet), q (quartet), and m (multiplet)], coupling-constants (Hz), and integration. The chemical shifts (δ) of ¹³CNMR (100 MHz) signals are reported in ppm relative TMS and using the solvent resonance as the internal standard.

	$ \begin{array}{c} $	TsOH•H ₂ O (20 mol%) or MgCl ₂ •6H ₂ O (10 mol%) or <u>CH₃ EtOH, 80 °C</u>	CH ₃ O CH ₃ CH ₃ N CH ₃ 3a	
Entry	Reaction conditions	<i>m</i> (1a)	m (3a)	Yield (%) ^b
1	А	5.0 g	7.0 g	94.6
2	В	5.0 g	7.2 g	97.3
3	C	5.0 g	6.8 g	91.9

^aReaction conditions **A**: **1a** (5.0 g), **2a** (7.4 g), TsOH · H₂O (1.41 g), and EtOH (50 mL) in air, 80 °C, 12 h; reaction conditions **B**: **1a** (5.0 g), **2a** (7.4 g), MgCl₂ · 6H₂O (0.75 g), and EtOH (3.0 mL) in air, 80 °C, 12 h; reaction conditions **C**: **1a** (5.0 g), **2a** (7.4 g), Cu

 $(NO_3)_2 \cdot 3H_2O$ (0.89 g), and EtOH (3.0 mL) in air, 80 °C, 12 h. ^bIsolated yield.

Procedure A

A mixture of 2-aminoaryl ketones 1 (0.50 mmol), β -ketoesters/ketones 2 (1.0 mmol), and 4-toluenesulfonic acid (TsOH \cdot H₂O, 19.0 mg, 0.10 mmol) in EtOH (3 mL) was added into a Schlenk flask (25 mL) and the mixture was stirred at 80 °C until the reaction was finished. Then the solvent was evaporated under reduced pressure and the residue was purified by column chromatography.

Procedure B

A mixture of 2-aminoaryl ketones 1 (0.50 mmol), β -ketoesters/ketones 2 (1.0 mmol), and magnesium chloride (MgCl₂ · 6H₂O, 20.3 mg, 0.10 mmol) in EtOH (3 mL) was added into a Schlenk flask (25 mL) and the mixture was stirred at 80 °C until the reaction was finished. Then the solvent was evaporated under reduced pressure and the residue was purified by column chromatography.

Procedure C

A mixture of 2-aminoaryl ketones 1 (0.50 mmol), β -ketoesters/ketones 2 (1.0 mmol), and cupric nitrate (Cu(NO₃)₂ · 6H₂O, 24.2 mg, 0.10 mmol) in EtOH (3 mL) was added into a Schlenk flask (25 mL) and the mixture was stirred at 80 °C until the reaction was finished. Then the solvent was evaporated under reduced pressure and the residue was purified by column chromatography.

1-(2,4-dimethylquinolin-3-yl)ethanone (3a):^[8e] Yield A:> 99%, 100.2 mg, B: >99%, 98.9 mg, C: >99%, 99.2 mg, light yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.92 (d, J = 8.4 Hz, 1H), 7.84 (dd, J = 8.4, 0.7 Hz, 1H), 7.62-7.58 (m, 1H), 7.45-7.41 (m, 1H), 2.54 (s, 3H), 2.49 (s, 3H), 2.46 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 206.6, 152.5, 146.8, 138.6, 135.6, 129.7, 129.1, 126.3, 125.9, 123.6, 32.6, 23.5, 15.2.

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