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One pot, Five-component Synthesis of Functionalized Piperidines Using $Zn(OAc)_2.2H_2O$ as a Highly Efficient Catalyst

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Abstract

A convenient synthetic route for the synthesis of biologically active functionalized piperidines using $Zn(OAc)_2.2H_2O$ as a highly efficient catalyst via five-component reaction of aromatic aldehydes, anilines and *β*-ketoesters at ambient temperature has studied. Mild reaction conditions, simplicity of operation and work-up procedures with no necessity of chromatographic purification steps, the availability and easy to handle of this solid catalyst and good to high yields are the notable benefits for the highly efficient synthesis of these products.

Keywords: *Zinc acetate dihydrate ($Zn(OAc)_2.2H_2O$), Functionalized piperidines, β-ketoesters, Aromatic aldehydes, Aniline derivatives.*

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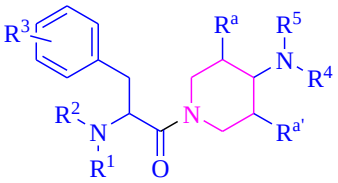
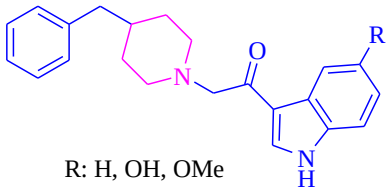
Introduction

Polyfunctionalized piperidines are widely distributed in naturally occurring monocyclic and bicyclic alkaloids and synthetic drugs [1]. Also, piperidine and its derivatives have an important role in drug discovery exhibiting various biological activities such as anti-hypertensive [2], antimalarial [3], neuro-protective [4, 5], antibacterial [6], anticonvulstant [7], and anti-inflammatory activities [8]. Furthermore, it is noteworthy that the substituted piperidines are important therapeutic agents in the treatment of influenza infection [9-11] diabetes [12, 13], viral infections, including AIDS [14, 15] and cancer metastatis [16, 17]. Besides, some of the tetrahydropyridine(THP) derivatives have been found to possess enzyme inhibitory activity versus farnesyltransferase [18] (Figure 1).

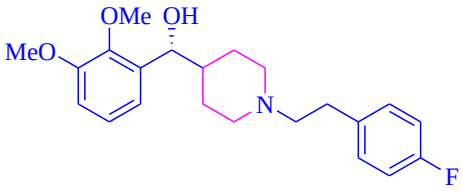


use for treatment of diabetes



R: H, OH, OMe

neuro-protective agent



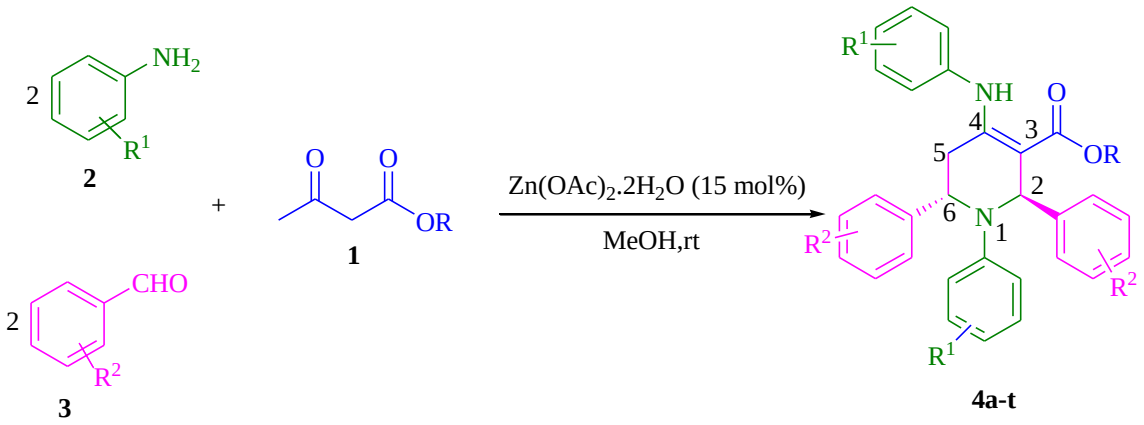
Antipsychotic agent

Figure 1. Pharmaceutically active compounds containing piperidine unit.

In the recent years, considerable attention has been paid to the design of efficient and environmentally friendly synthetic route by using of multi component domino reactions (MCRs) [19-27] due to a wide range points such as atom-economy, simple work-up, mild and environmentally-friendly, one-pot and low-cost.

Due to the importance of Poly functionalized piperidines, various methodologies for the preparation of these compounds have developed such as VCl_3 [28], $BF_3.SiO_2$ [29], Ph_3CCl [30], $LaCl_3.7H_2O$ [31], tartaric acid [32], iodine [33], $ZrOCl_2.8H_2O$ [34], $ZrCl_4$[35], $InCl_3$ [36], tetrabutylammoniumtribromide (TBATB) [37], $Bi(NO_3)_3.5H_2O$ [38], bromodimethylsulfonium bromide (BDMS) [39], cerium ammonium nitrate (CAN) [40], *p*-$TsOH{\cdot}H_2O$ [41]. Some of limitation these methodologies are low yields, toxic catalyst, harsh reaction conditions, expensive materials and longer time reactions. Therefore, as a part of our research aimed at the expansion of a

simple and high-yielding environmentally benign procedure for the one-pot multi-component synthesis of piperidines without these problems. During the past decades, the use of zinc compounds as environmental safe catalysts in organic synthesis have attracted great interest due to their notable advantages such as non-toxic, easy to handle, highly efficient and low-cost [42- 43]. Efficient, readily, low-cost and non- toxic catalyst, good to high yields, short reaction times and eco-friendly make our protocol alternative in comparison to some of the earlier reported methods. Also $Zn(OAc)_2.2H_2O$ can be successfully used in the type of carbon-carbon bonds as an available, eco-friendly and environmentally friendly catalyst [45, 46] in organic synthesis and herein, we report here a facility and eco-friendly protocol for the synthesis of highly substituted piperidines via a one-pot five-component reaction between aromatic aldehydes, anilines and *β*-ketoesters in the presence of $Zn(OAc)_2.2H_2O$ as a catalyst in methanol at ambient temperature (Scheme 1). Highly effective, readily, low-cost and non-toxic catalyst, good to high yields, short reaction times and eco-friendly that make our protocol alternative in comparison to some of the earlier reported methods.



Scheme 1. Synthesis of highly substituted piperidine.

Experimental

General

Melting points and IR spectra all compounds were determined using an Electro thermal 9100 apparatus and a JASCO FTIR 460 Plus spectrometer. Also, nuclear magnetic resonance, ^1H NMR spectra were recorded on a Bruker DRX-400 Avance instrument with $CDCl_3$ as solvent. All reagents and solvents were purchased from Merck, Fluka and Acros chemical companies were used without further purification.

General procedure for the synthesis of highly functionalized piperidine **(4a-t)**

A solution of aromatic amine **2** (2.0 mmol) and *β*-ketoester **3** (1.0 mmol) in MeOH (5 mL) was stirred for 20 min in the presence of 15 mol% $Zn(OAc)_2.2H_2O$ at room temperature. Next, the aromatic aldehyde **1** (2.0 mmol) was added and the reaction mixture was stirred for the time indicated in Table 2. The progress of the reaction was monitored by thin-layer chromatography (TLC). After completion of the reaction, the thick precipitate was filtered off and washed with ethanol (3 × 2 mL) to give the pure product **4**. The catalyst is solvable in ethanol and was removed from the reaction mixture. The products were characterized by comparison of spectroscopic data (^{1}HNMR). Spectra data products are represented below:

Methyl-1-phenyl-4-(phenylamino)-2,6-bis(4-chlorophenyl)1,2,5,6-tetrahydropyridine-3-carboxylate **(4c)**

Solid powder; m.p. 191-193°C; ^{1}HNMR (400 MHz, $CDCl_3$): δ 2.75 (1H, dd, *J* = 15.2, 2.4 Hz, H′-5), 2.86 (1H, dd, *J* = 15.2, 5.6 Hz, H″-5), 3.94 (3H, s, OCH_3), 5.11 (1H, d, *J* = 3.6 Hz, H-6), 6.39 (2H, d, *J* = 7.8 Hz, ArH), 6.40 (1H, s, H-2), 6.56 (2H, d, *J* = 8.0 Hz, ArH), 6.64 (1H, t, *J* = 7.0 Hz, ArH), 7.04–7.27 (13H, m, ArH), 10.26 (1H, s, NH).

Methyl -1-phenyl-4-(phenylamino)-2,6-bis(4-methylphenyl)-1,2,5,6-tetrahydropyridine-3-carboxylate **(4e)**

Solid powder; m.p. 213-215°C; ^{1}HNMR (400 MHz, $CDCl_3$): δ 2.25 (3H, s, CH_3), 2.32 (3H, s, CH_3), 2.75 (1H, dd, *J* = 15.2, 2.4 Hz, H′-5), 2.84 (1H, dd, *J* = 15.2, 5.6 Hz, H″-5), 3.93 (3H, s, OCH_3), 5.09 (1H, d, *J* = 3.1 Hz, H-6), 6.32 (2H, d, *J* = 8.0 Hz, ArH), 6.37 (1H, s, H-2), 6.48 (2H, d, *J* = 8.8 Hz, ArH), 6.60 (1H, t, *J* = 7.2 Hz, ArH), 7.00–7.12 (11H, m, ArH), 7.20 (2H, d, *J* = 8.0 Hz, ArH), 10.29 (1H, s, NH).

Methyl 4-(4-methylphenylamino)-1-(4-fluorophenyl)-1-(4-methylphenyl)-1,2,5,6-tetrahydro-2,6-diptolylpyridine-3-carboxylate **(4l)**

Solid powder; m.p. 204-206°C; IR (KBr) ν = 3264 (NH), 1658 (C=O) cm^{-1}; ^{1}HNMR (400 MHz, $CDCl_3$) δ (ppm): 2.20 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 2.75 (dd, 1H, *J* = 15.1, 2.4 Hz, H′-5), 2.83 (dd, 1H, *J* = 15.1, 5.6 Hz, H″-5), 3.95 (s, 3H, OCH_3), 5.11 (br s, 1H, H-6), 6.31 (d, 2H, *J* = 8.4 Hz, ArH), 6.37 (s, 1H, H-2), 6.42 (d, 2H, *J* = 8.8 Hz, ArH), 6.92 (d, 2H, *J* = 8.4 Hz, ArH), 7.97–7.02 (m, 6H, ArH), 7.12–7.15 (m, 2H, ArH), 7.27–7.31 (m, 2H, ArH), 10.22 (s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 20.1 (CH_3), 33.7 (C-5), 51.0 (OCH_3), 54.7 (C-2), 57.3 (C-6), 97.2 (C-3), 113.0, 114.9 (d, J= 21.0 Hz), 115.4 (d, J= 21.0 Hz), 125.6, 125.8, 127.9 (d, J= 8.0 Hz), 128.2 (d, J=

7.0 Hz), 129.6, 135.0, 135.9, 138.4, 139.7, 144.5, 156.4 (C-4), 161.5 (d, $^1J_{CF}$ = 243.0 Hz), 161.9 (d, $^1J_{CF}$ = 244.0 Hz), 168.4 (C=O).

Methyl-1-phenyl-4-(4-chlorophenylamino)-2,6-bis(4-methoxyphenyl)-1,2,5,6 tetrahydropyridine-3-carboxylate **(4o)**

Solid powder; m.p. 192-194°C; ^{1}HNMR (400 MHz, $CDCl_3$): δ 2.71 (1H, dd, *J*= 15.2, 2.4 Hz, H′-5), 2.86 (1H, dd, *J*= 15.2, 5.6 Hz, H″-5), 3.81, 3.83, 3.97 (9H, 3s, $3OCH_3$), 5.07 (1H, d, *J*= 3.6 Hz, H-6), 6.28 (2H, d, *J*= 8.0 Hz, ArH), 6.32 (1H, s, H- 2), 6.46 (2H, d, *J*= 8.0 Hz, ArH), 6.83-7.20 (12H, m, ArH), 10.25 (1H, s, NH).

Ethyl 4-(4-bromophenylamino)-1-(4-bromophenyl)-1,2,5,6-tetrahydro-2,6-diptolylpyridine-3-carboxylate **(4t)**

Solid powder; m.p. 233-235°C; IR (KBr) ν = 3310 (NH), 1652 (C=O) cm^{-1}; ^{1}HNMR (400 MHz, $CDCl_3$) δ (ppm): 1.49 (t, 3H, *J* = 6.8 Hz, OCH_2CH_3), 2.35 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 2.74 (d, 1H, *J* = 15.2 Hz, H′-5), 2.88 (dd, 1H, *J* = 15.2, 5.6 Hz, H″-5), 4.33-4.39 (m, 1H, OCH_aH_b), 4.45–4.51 (m, 1H, OCH_aH_b), 5.09 (d, 1H, *J* = 3.6 Hz, H-6), 6.17 (d, 2H, *J* = 8.0 Hz, ArH), 6.35 (s, 1H, H-2), 6.42 (d, 2H, *J* = 8.8 Hz, ArH), 7.05–7.24 (m, 12H, ArH), 10.26 (s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 14.7 (OCH_2CH_3), 21.0 (CH_3), 21.2 (CH_3), 33.4 (C-5), 55.0 (C-2), 58.1 (C-6), 59.9 (OCH_2CH_3), 99.0 (C-3), 108.2, 114.5, 118.9, 126.2, 126.4, 127.2, 129.0, 129.4, 131.5, 131.9, 136.1, 137.0, 139.1, 140.2, 146.0, 155.2 (C-4), 168.1 (C=O).

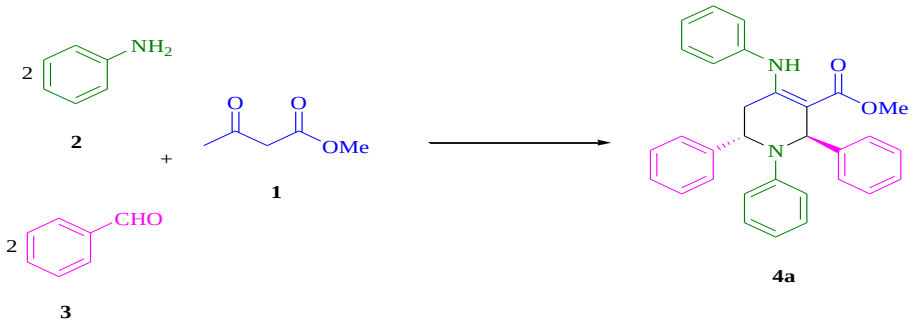
Results and Discussion

Initially, for optimizing the reaction conditions, the one-pot five-component reaction between benzaldehyde, aniline and methyl acetoacetate was tested as a model reaction at ambient temperature (Table 1). And a control experiment revealed that in the absence of the catalyst, no product was obtained after 24 h, which indicated that the catalyst's presence is necessary for this reaction (Table 1, entry 1). To further optimize reaction conditions, we investigated the effect of the loading amount of $Zn(OAc)_2.2H_2O$ on the model reaction in methanol (Table 1). The optimum yield of product **4a** (84%) was obtained in the presence of 15 mol% of $Zn(OAc)_2.2H_2O$ (Table 1, entry 4). By lowering the catalyst loading to 5 mol%, the corresponding product was obtained in lower yield(Table 1, entry 2). While increasing the catalyst loading to 20 mol% has no significant effect on the product yield (Table 1, entry 11). Subsequently, a survey of solvents showed methanol to be the best choice (Table 1, entry 4). Low yields were obtained when the model reaction was performed in EtOH, H_2O, CH_3CN, CH_2Cl_2, $CHCl_3$ (Table 1). Also, when the reaction was

performed under solvent-free conditions, the product was generated in a low yield (Table 1, entry 5). Thus, Different reactions between substituted anilines, aldehyde derivatives, and methyl/ethyl acetoacetate were examined under the optimized conditions reaction to give the corresponding piperidines in good to high yields, and the results are summarized in Table 2.

The structure of the products was characterized by their melting points and nuclear magnetic resonance (^{1}H NMR) spectral data, which were then compared with those of authentic samples.

Table1. Optimization of the reaction condition on the synthesis of **4a** [a].



Entry	Zn(OAc)$_2$.2H$_2$O (mol %)	Solvent	Time (h)	Isolated Yields (%)
1	Catalyst free	MeOH	24	Not product
2	5	MeOH	24	31
3	10	MeOH	12	59
4	**15**	**MeOH**	**7**	**84**
5	15	Solvent free	24	27
6	15	EtOH	12	52
7	15	H_2O	24	trace
8	15	CH_3CN	12	43
9	15	CH_2Cl_2	24	21
10	15	$CHCl_3$	24	16
11	20	MeOH	4	86

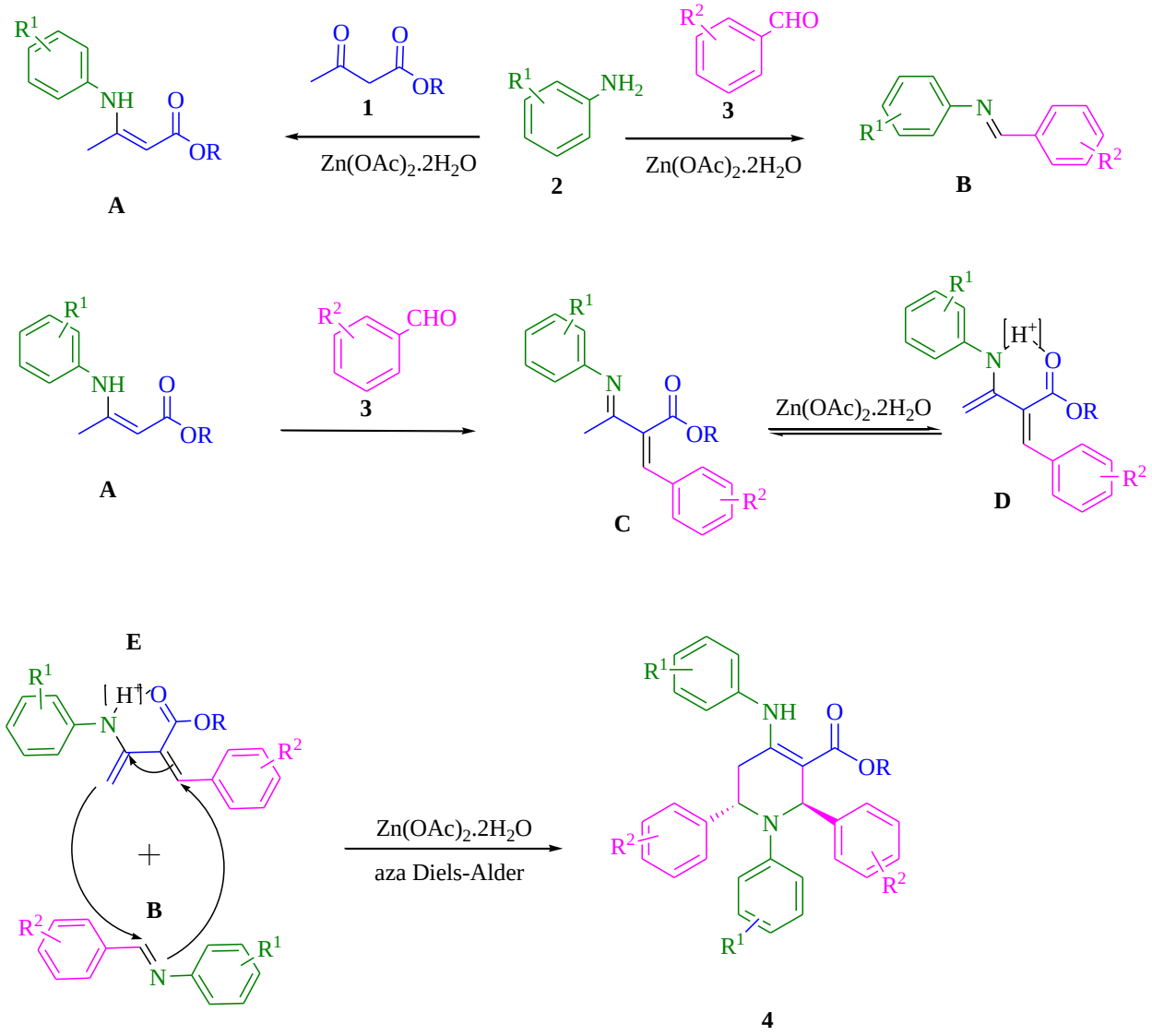
[a]Reaction conditions: benzaldehyde (2 mmol), aniline (2 mmol), and methyl acetoacetate (1 mmol) and catalyst in various solvents at room temperature.

Table 2. Synthesis of highly substituted piperidines.

Entry	R^1	R^2	R	Product	Time (h)	Yield (%)[a]	m.p. ˚C	Lit. m.p. ˚C
1	H	H	Me	**4a**	7	84	171-173	169-171[35]
2	H	H	Et	**4b**	7	81	175-177	173-175[35]
3	H	4-Cl	Me	**4c**	8	86	191-193	189-191[39]
4	4-Cl	H	Et	**4d**	7	79	201-203	203-205[35]
5	H	4-Me	Me	**4e**	6	83	213-215	212-214[39]
6	4-Me	4-Me	Me	**4f**	6	89	204-206	204-207[35]
7	4-Me	4-Me	Et	**4g**	6	86	168-170	169-171[35]
8	H	4-OMe	Me	**4h**	7	87	185-187	187-188[39]
9	H	4-OMe	Et	**4i**	8	85	164-166	166-168[35]
10	H	4-F	Me	**4j**	5	91	180-182	180[41]
11	4-OMe	4-F	Me	**4k**	6	89	205-207	204-205[40]
12	4-Me	4-F	Me	**4l**	5	93	204-206	203-205[32]
13	4-F	4-Me	Et	**4m**	5	92	185-187	186-187[32]
14	4-Cl	4-Me	Et	**4n**	6	85	217-219	218-220[29]
15	4-Cl	4-OMe	Me	**4o**	6	82	192-194	194-195[40]
16	H	4-NO_2	Me	**4p**	5	85	240-242	239-241[33]
17	H	4-NO_2	Et	**4q**	5	81	248-250	247-250[40]
18	4-Cl	4-Br	Me	**4r**	8	79	162-164	160-163[34]
19	4-Me	H	Et	**4s**	5	86	198-200	196-198[38]
20	4-Br	4-Me	Et	**4t**	7	83	233-235	234-236[29]

[a] Isolated yield.

And proposed mechanistic route for the synthesis of highly substituted piperidines in the presence of zinc acetate dihydrate are shown in scheme 2. Zinc acetate dihydrate, as a catalyst for the construction of imine **B** formed by the reaction of aromatic aldehyde with aniline. Subsequently, ethyl acetoacetate reacts with aniline to give *β*-enaminone **A**. Benzaldehyde which is retained in the reaction mixture undergoes Knoevenagel condensation with *β*-enaminone leading to the formation of intermediate **D** and reactive form **E**. Due to the diene core present in intermediate **E**, it proceeds towards an intramolecular [4+2] aza-Diels-Alder reaction with imine **B** (serves as dienophile) which affords the foreseen functionalized piperdine **4** (Scheme 2).



Scheme 2. Proposed mechanistic route for the synthesis of highly substituted piperidines.

Comparison of catalytic ability of some catalysts reported in the literature for the synthesis of highly substituted piperidines are shown in Table 3.

Table 3. Comparison of catalytic ability some of catalysts reported in the literature for synthesis of piperidines [a]

Entry	Catalyst	Conditions	Time/Yield (%)	References
1	Ph_3CCl	MeOH, 50 °C	5 h/79	[30]
2	Tartaric acid	MeOH, r.t.	14 h/79	[32]
3	I_2	MeOH, r.t.	8 h/81	[33]
4	$ZrOCl_2.8H_2O$	EtOH, reflux	3.5 h/80	[34]
5	$ZrCl_4$	EtOH, r.t.	9 h/90	[35]
6	$InCl_3$	CH_3CN, r.t.	24 h/60	[36]
7	TBATB	EtOH, r.t.	24 h/74	[37]
8	$Bi(NO_3)_3.5H_2O$	EtOH, r.t.	12 h/81	[38]
9	BDMS	CH_3CN, r.t.	3 h/75	[39]
10	CAN	CH_3CN, r.t.	20 h/82	[40]
11	$Zn(OAc)_2.2H_2O$	MeOH, r.t.	7 h/84	This work

[a]Based on the five-component reaction of benzaldehyde (2 mmol), aniline (2 mmol), and methyl acetoacetate (1 mmol).

Conclusion

In summary, a clean and eco-friendly protocol presented for the one-pot, five-component preparation of highly functionalizaed piperidines under ambient reaction conditions using $Zn(OAc)_2.2H_2O$ as the catalyst in methanol with short reaction times. The present procedure provides an economic and simple methodology for the synthesis of a target compound. And offer several notable advantages over the existing methods, including eco-friendly, low-cost, available and non-toxic catalyst, clean reaction profiles, good to high yields, purification of products without the need of column chromatography.

Acknowledgements

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