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Efficient Synthesis of Dihydropyrimidine and Amidoalkyl Naphthol Derivatives Using Zinc Chloride-Based Deep Eutectic Systems as Solvent & Catalyst

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Abstract

Dihydropyrimidine and amidoalkyl naphthol derivatives have been prepared efficiently in a one-pot synthesis using $ZnCl_2$/urea and $ZnCl_2$/acetamide deep eutectic systems as reaction medium and homogeneous catalyst. This method offers some advantages such as simple procedure, inexpensive solvent and catalyst and good yields of the final products in short reaction times. The use of non-toxic and environmentally benign catalyst and solvent system are the main remarkable features of this procedure.

Keywords: Deep eutectic; 3, 4-dihydropyrimidine; Amidoalkylnaphthol; Homogeneous catalyst.

Introduction

The main disadvantages of organic solvents are their environmental pollution, cost and flammability. One of the most important aims of green chemistry is to design chemical processes so as to eliminate or reduce the use of toxic and volatile organic solvents.

Through all the possible choices to reduce chemical pollution, ionic liquids (ILs) have attracted much attention due to their numerous advantages. IL, a unique alternative for organic solvents, is not only recyclable, stable and non-flammable, but also shows low vapor pressure. Unfortunately, some impediments, such as high cost and toxicity [1] have limited the chemical and industrial usage of ILs. On the other hand, deep eutectic solvents (DESs) are suitable alternatives. DESs are based on a combination of readily available and inexpensive components that are formed by mixing a quaternary ammonium salt or a metal salt with a simple hydrogen bond donor (HDB), such as urea, a carboxylic acid or a Lewis acid. Since their polar nature often makes DESs immiscible with organic solvents, work-up is easy. Furthermore, DESs show novel reactivity and selectivity for highly efficient synthesis of pharmaceutical products, agrochemicals, and natural products [2–4].

A multicomponent reaction (MCR) is a process in which three or more easily accessible components are combined together in a single reaction vessel to produce a final product displaying features of all inputs and thus offers greater possibilities for molecular diversity per step with a minimum of synthetic time and effort [5].

3,4- Dihydropyrimidin- 2-(1H)- ones (Biginelli Products) are very important heterocyclic systems due to their interesting biological activities such as antitumour, antibacterial, antiviral and anti-inflammatory activities [6]. The classical synthesis of dihydropyrimidines (DHPMs) was first reported by the

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Italian chemist Pietro Biginelli in 1893, involving a one pot condensation of an aldehydes, β-ketoester and urea under strongly acidic conditions. However, this method suffers from low yields (20–40%) of desired products.

This has led to the disclosure of several one-pot methodologies for the synthesis of DHPM derivatives such as [bmim] [$FeCl_4$] [7], piperidinium triflate [8], $Al(NO_3)_3 \cdot 9H_2O$ [9] and cellulose sulfuric acid [10].

The preparation of 1-amidoalkyl-2-naphthols can be carried out by multi-component condensation of aryl aldehydes, 2-naphthol and an amide in the presence of Lewis or Brønsted acid catalysts such as tin dioxide [11], $KAl(SO_4)_2 \cdot 12H_2O$ [12], and iodine [13].

One of the major drawbacks of these reactions is that in some cases when a heterogeneous catalyst is used an organic solvent such as dichloromethane is needed for the extraction of product from catalyst. This problem can be solved by using of eco-friendly solvents such as deep eutectic sytems.

On the other hand, some of the existing methods displayed drawbacks, such as environmental pollution caused by performing of the reaction in organic solvents, long reaction time, exotic reaction conditions, high cost or very acidic catalysts. Therefore, the development of a new methodology and high yielding catalytic process is desired that could overcome the above drawbacks.

Materials and Methods

All chemicals were purchased from Merck chemical company and were used without further purification. All products are known and were identified by comparison of their spectral data and physical properties with those of the authentic samples. Melting points were obtained in open capillary tubes and were measured on an Electrothermal-9100 apparatus. IR spectra were recorded on a Brucker Tensor-27 FTIR spectrometer. ^1H and ^{13}C NMR spectra were determined on a Bruker DRX-400 Avance instrument at 400 and 100 MHz.

Preparation of Deep Eutectic Solvents

The deep eutectic solvents were prepared as described in the literature [14]: urea (3.5 mmol) was mixed with zinc chloride (1 mmol) and heated at 100 ^oC in air with stirring until a clear colorless liquid was obtained. Then the mixture was used. The same procedure was used for acetamide:$ZnCl_2$ deep eutectic mixture.

General procedure for the preparation of dihydropyrimidines

A mixture of an aldehyde (1 mmol), acetoacetate derivative (1.2 mmol) and urea:$ZnCl_2$ DES (3.5:1 mmol) was heated at 80 ^oC for a period of time as indicated in Table 1. The reactions were followed by thin layer chromatography (TLC). After completion of the reaction, 10 mL of water was added to the mixture and the resulting precipitate was filtered off. The product was recrystalyzed from ethanol.

General procedure for the preparation of amidoalkyl naphthols

A mixture of an aldehyde (1 mmol), 2-naphthol (2 mmol) and acetamide:$ZnCl_2$ DES (4:1 mmol) was heated at 120 ^oC for a period of time as indicated in Table 5. The reactions were followed by thin layer chromatography (TLC). After completion of the reaction, 10 mL of water was added to the mixture and the resulting precipitate was filtered off. The product was recrystalyzed from ethanol.

6-Methyl-2-oxo-4-phenyl-1, 2, 3, 4-tetrahydro-pyrimidine-5-carboxylic acid methyl ester (table 2, compound 12a):

IR (KBr) ν_{max}: 3333, 3223, 1696, 1667 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) 2.25 (s, 3H, CH_3), 3.53 (s, 3H, OCH_3), 5.15 (d, J = 2.8 Hz, 1H, CH), 7.23 - 7.33 (m, 5H, arom), 7.76 (d, J = 3.2 Hz, 1H, NH), 9.22 (s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 17.7, 50.7, 53.6, 98.9, 126.1, 127.2, 128.4, 144.6, 148.6, 152.1, 165.7.

6-Methyl-2-oxo-4-p-tolyl-1, 2, 3, 4-tetrahydro-pyrimidine-5-carboxylic acid methyl ester (table 2, copmpound 14a):

IR (KBr) ν_{max}: 3367, 3220, 1702, 1644 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) : δ (ppm) 2.24 (s, 3H, CH_3) , 2.26 (s, 3H, CH_3) , 3.52 (s, 3H, OCH_3), 5.10 (d, J = 3.2 Hz , 1H, CH), 7.12 (m, 4H, arom) 7.73 (d, J = 2.4 Hz , 1H, NH), 9.20 (s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 17.7, 20.6, 50.7, 53.4, 99.0, 126.0, 128.9, 136.9, 141.7, 148.4, 152.1, 165.8.

6-Methyl-2-oxo-4-o-tolyl-1, 2, 3, 4-tetrahydro-pyrimidine-5-carboxylic acid methyl ester (table 2, copmpound 16a):

IR (KBr) ν_{max}: 3238, 3103, 2932, 1692, 1644 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) : δ (ppm) 0.99 (t, J = 7.2 Hz, 3H, CH_3) , 3.88 (m, 2H, CH_2), 5.40 (d, J = 2.8 Hz, 1H, CH), 7.12-7.17 (m, 4H, arom) , 7.65 (s, 1H, NH), 9.17 (s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 13.8, 17.6, 18.6, 50.3, 59.0, 99.1, 126.9, 127.1, 130.0, 139.6, 143.2, 148.3, 148.4, 151.5, 165.2.

N-[(2-Hydroxy-naphthalen-1-yl)-phenyl-methyl]-acetamide (table 5, compound 1b):

IR (KBr) ν_{max}: 3244, 1687, 1639 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) 1.98 (s, 3H, CH_3), 7.15-7.37 (m, 9H), 7.75-7.81 (m, 3H), 8.44 (d, *J* = 8.0 Hz, 1H), 9.99 (s, 1H, OH).

^{13}C NMR (100 MHz, DMSO–d_6): δ (ppm) 22.6, 47.7, 118.4, 118.7, 122.3, 123.1, 123.2, 125.9, 126.9, 127.9, 128.4, 125.5, 129.1, 132.1, 142.5, 153.1, 169.2.

N-[(2-Hydroxy-naphthalen-1-yl)-p-tolyl-methyl]-acetamide (table 5, compound 2b):

IR (KBr) ν_{max}: 3397, 1687, 1626 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) : δ (ppm) 1.96 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 7.08 (d, *J* = 6.8 Hz, 2H), 7.20 (d, *J* = 8.8 Hz, 2H), 7.25 (t, *J* = 7.2 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.83 (s, 1H, NH), 8.40 (d, *J* = 8.4 Hz, 1H), 9.96 (s, 1H, OH). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 20.5, 22.6, 47.5, 118.3, 118.3, 120.3, 123.2, 123.3, 123.4, 125.9, 126.2, 128.5, 129.1, 132.2, 134.9, 139.5, 153.0, 169.1.

Results and Discussion

In this study, we used urea/$ZnCl_2$ and acetamide/$ZnCl_2$ deep eutectic systems for the synthesis of 3, 4-dihydropyrimidine-2(1*H*)-ones and amidoalkyl napththols (scheme 1).

Since these syntheses typically require acidic conditions, we have investigated melt systems consisting of a lewis acid as one of the melt components and one of the reactants as the other component.

For the synthesis of biginelli dihydropyrimidines, urea/$ZnCl_2$ eutectic system was choosed as both solvent and a homogeneous catalyst.

To optimize the conditions, the reaction of benzaldehyde, ethyl acetoacetate was selected as a model to investigate the effects of different amounts of deep eutectic solvent and temperature on the yield. As table 1 shows the best result was obtained by carrying out the reaction with 1mmol of benzaldehyde, 1.2 mmol of ethyl acetoacetate and 3.5:1 mmol of urea:$ZnCl_2$ at 80°C.

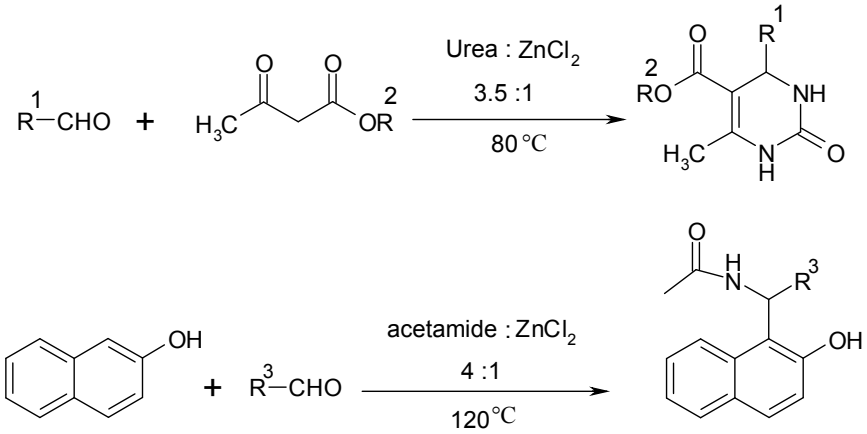
With these optimized conditions, the scope of this synthesis in deep eutectic solvent was investigated using various aldehydes. The results are summarized in Table 2.

All the aromatic aldehydes reacted smoothly to give good yields of the products, except 4-N, N-dimethylaminobenzaldehyde which gave no product (Table 2, entry 11a). It seems amino group of aldehyde reacts with $ZnCl_2$ and deactivates it.

In order to evaluate the ability of the present method with respect to the reported methods for the preparation of 3, 4-dihydropyrimidine-2(1*H*)-ones, the synthesis of compound 1a was compared with the reported methods with similar conditions (Table 3). As it is clear from Table 3, the present method is more efficient.

A proposed reaction mechanism for the synthesis of Biginelli dihydropyrimidines using $ZnCl_2$/urea deep eutectic system is presented in Scheme 2. The reaction of the aldehydes and urea generates an acylimine intermediate (A). Interception of this iminium ion intermediate by activated 1, 3-dicarbonyl compound produces an open-chain ureide (B) which subsequently undergoes cyclization and dehydration to afford the corresponding dihydropyrimidinone (C).

After successfully synthesizing a series of dihydropyrimidines, we focused our attention on the synthesis of amidoalkyl naphthol derivatives using acetamide/$ZnCl_2$ as a deep eutectic solvent. In order to synthesis of amidoalkyl naphthols in an efficient way, a

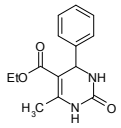
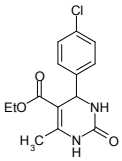
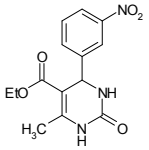
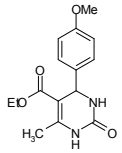
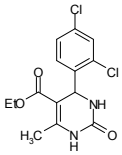
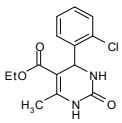
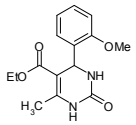
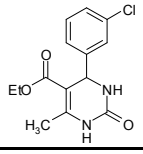


Scheme1. Synthesis of dihydropyrimidines and amidoalkyl napththols using $ZnCl_2$ based deep eutectic solvents

Table 1. Optimization conditions for the synthesis of 3, 4-dihydropyrimidine-2(1*H*)-ones

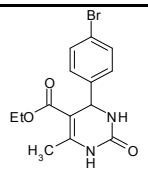
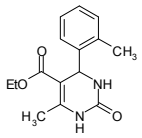
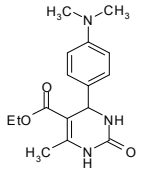
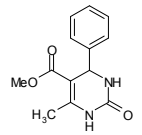
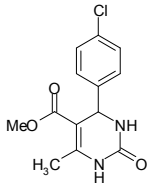
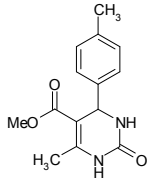
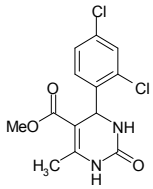
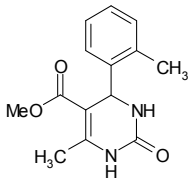
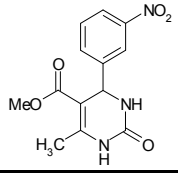
Time (min)	Temperature (^oC)	Yield (%)	Urea: $ZnCl_2$	Ethyl acetoacetate (mmol)
50	60	60	3.5:1	1
30	70	75	3.5:1	1
10	80	90	3.5:1	1
10	90	91	3.5:1	1
7	**80**	**96**	**3.5:1**	**1.2**
8	90	95	3.5:1	1.2
7	80	95	3.5:1	1.5
7	80	96	7:2	1.2

Table 2. Synthesis of 3, 4-dihydropyrimidine-2(1*H*)-one derivatives in the presence of urea:$ZnCl_2$ deep eutectic solvent

Entry	R^1	R^2	Product	Time (min)	Yield (%)	Observed mp (^oC)	Reported mp (^oC)	Ref.
1a	C_6H_5	OEt		7	96	205-207	203-205	15
2a	4-(Cl)-C_6H_5	OEt		7	92	208-210	210-212	15
3a	3-(NO_2)-C_6H_5	OEt		7	85	225-227	225-226	20
4a	4-(OCH_3)-C_6H_5	OEt		14	76	207-209	203-204	15
5a	2,4-($Cl)_2$-C_6H_5	OEt		10	91	244-246	246-248	16
6a	2-(Cl)-C_6H_5	OEt		7	95	218-220	227-229	15
7a	2-(OCH_3)-C_6H_5	OEt		5	90	260-263	256-258	15
8a	3-(Cl)-C_6H_5	OEt		10	88	188-190	195-197	15

series of reactions using acetamide/$ZnCl_2$ as both solvent and catalyst were run under different conditions. The results of optimization experiments involving a 1:1 ratio of 2-naphthol and benzaldehyde in a one-pot

Table 2. Cntd

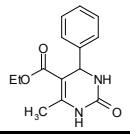
9a	4-(Br)-C_6H_5	OEt		7	95	220-222	213-215	17
10a	2-(CH_3)-C_6H_5	OEt		7	95	201-203	207-208	18
11a	4–$N(CH_3)_2$–C_6H_5	OEt		60	0	-	-	-
12a	C_6H_5	OMe		5	93	214-216	208-211	17
13a	4-(Cl)-C_6H_5	OMe		7	90	207-210	206-208	15
14a	4-(CH_3)-C_6H_5	OMe		10	96	207-210	210-213	16
15a	2,4-$(Cl)_2$-C_6H_5	OMe		7	92	253-254	254-255	15
16a	2-(CH_3)-C_6H_5	OMe		12	89	232-235	239-242	20
17a	3-(NO_2)-C_6H_5	OMe		12	90	261-263	279-280	18

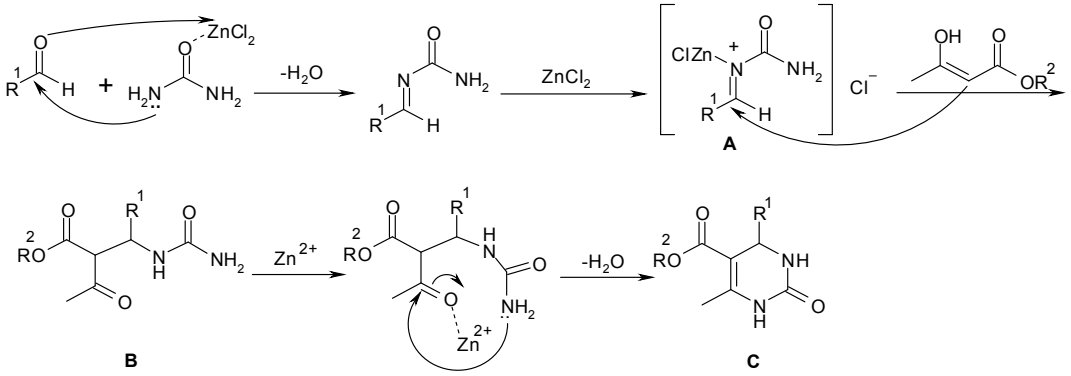
condensation reaction are presented in Table 4.

As table 4 shows the best result was obtained by carrying out the reaction with 1 mmol of 2-naphthol, 1 mmol of benzaldehyde and 4:1 mmol of acetamide: $ZnCl_2$ at 120^oC.

With optimized conditions in hand we decided to

Table 3. Synthesis of dihydropyrimidine **1a** using different catalysts and reaction conditions

Product	Catalyst	Conditions	Time (min)	Yield (%)	Ref.
	$Al(NO_3)_3.9H_2O$	Solvent- Free 80°C	90	90	9
	$[Et_3NH]$ $[HSO_4]$	Solvent- Free 100°C	80	85	22
	Cellulose sulfuric acid	H_2O 100°C	300	80	10
	-	$ZnCl_2$/Urea 80°C	7	96	This work



Scheme 2. A reasonable mechanism for $ZnCl_2$/urea-catalyzed Biginelli reaction

explore the scope and limitations of this method. Thus, series of amidoalkyl naphthol derivatives with significant steric, electron withdrawing and donating substituents were synthesized and the obtained results are summarized in Table 5.

In all cases, aromatic aldehydes with substituents carrying either electron-donating or electron-withdrawing groups reacted successfully and gave the products in high yields. From the results of table 5 it is obvious that the electron-donating groups decrease the reaction rates as would be expected. Ortho-substituted aldehydes such as 2-methyl and 2-chlorobenzaldehyde, were studied and the results showed that the steric hindrance also affect the reaction rate.

To assess the privilege of the present method with respect to the literature methods for the preparation of the amidoalkyl naphthols, the synthesis of compound **1b** was compared with the reported methods with similar conditions (Table 6). As it is clear from Table 6, the present method is more efficient.

A reasonable mechanism for the formation of amidoalkyl napthol derivatives in the presence of $ZnCl_2$/acetamide eutectic system is shown in scheme 3. First reaction of β-naphthol with aromatic aldehydes in the presence of Zn^{2+} gives ortho-quinone methides (O-QMs). Then nucleophilic addition of acetamide to this O-QM intermediate this will give to the final amidoalkyl napthol.

Conclusion

In summary, this paper describes a convenient and efficient process for the synthesis of dihydropyrimidine and amidoalkyl naphthol derivatives employing $ZnCl_2$-based deep eutectic systems as reaction medium. Present methodology offers very attractive features such as reduced reaction times, higher yields and economic viability of the catalyst, when compared with conventional method as well as with other catalysts, which will have wide scope in organic synthesis. The simple procedure combined with the use of inexpensive, non-toxic and environmentally benign catalyst and

Table 4. Optimization conditions for the reaction of 2-naphthol and benzaldehyde

Time (min)	Temperature (°C)	Yield (%)	Acetamide: $ZnCl_2$
70	70	51	4:1
30	80	69	4:1
15	100	90	4:1
8	110	93	4:1
8	**120**	**96**	**4:1**
8	130	96	4:1
8	120	96	8:2

Table 5. Synthesis of amidoalkylnaphthol derivatives in the presence of acetamide:$ZnCl_2$ deep eutectic solvent

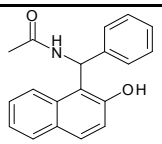
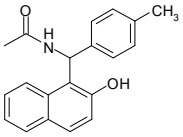
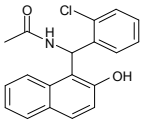
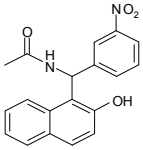
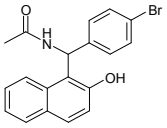
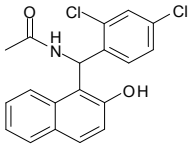
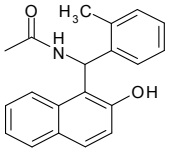
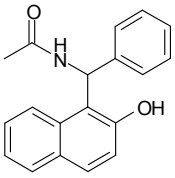
Entry	R^3	product	Time (min)	Yield (%)	Mp(observed) (^oC)	Mp(reported) (^oC)	Ref.
1b	C_6H_5		8	96	242-244	238-240	23
2b	4-(CH_3)- C_6H_5		12	92	211-214	226-229	12
3b	2-(Cl)-C_6H_5		12	80	199-202	198-200	12
4b	3-(NO_2)-C_6H_5		12	95	243-245	238-240	23
5b	4-(Br)-C_6H_5		6	91	227-230	225-227	12
6b	2,4-($Cl)_2$-C_6H_5		10	95	205-207	197-200	23
7b	2-(CH_3)-C_6H_5		20	92	214-217	197-199	24

Table 6. Synthesis of amidoalkylnaphthol **1b** using different catalysts and reaction conditions

Product	Catalyst	Conditions	Time (min)	Yield (%)	Ref.
	[PCl_3-n(SiO_2)n]	Solvent-Free 120 ^oC	20	93	24
	I_2	Solvent-Free 125 ^oC	330	85	13
	[TEBSA][HSO_4]	120 ^oC	10	87	25
	-	$ZnCl_2$/Acetamide 120 ^oC	8	96	This work

solvent system make this method economic, and a waste-free chemical process for the synthesis of dihydropyrimidine and amidoalkyl naphthol derivatives. The eutectic solvent and catalyst system can be prepared easily with readily available inexpensive reagents, which are non-hazardous.

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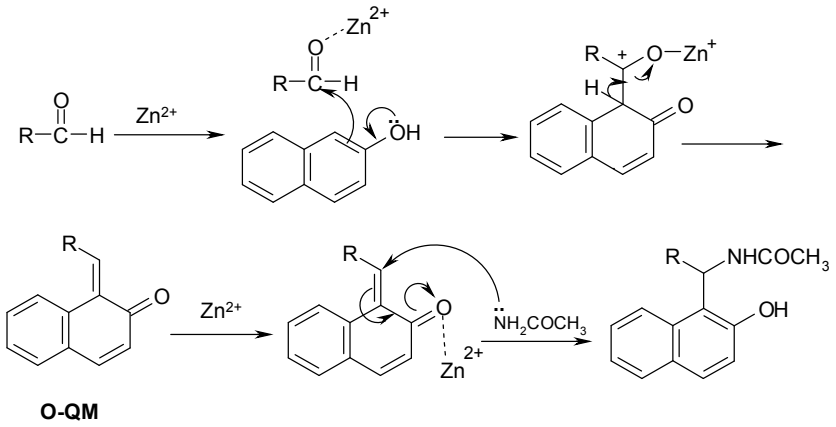

Scheme 3. A reasonable mechanism for the formation of amidoalkyl napthol derivatives in the presence of $ZnCl_2$/acetamide eutectic system

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