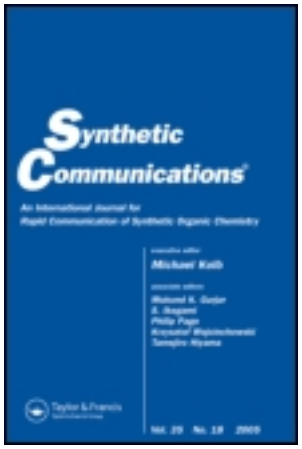

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High-Yield Method for the Preparation of 1,3,4,5-Tetrahydro-7-methoxy-2H-1-benzazepin-2-one with Excellent Regio- and Stereoselectivity

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HIGH-YIELD METHOD FOR THE PREPARATION OF 1,3,4,5-TETRAHYDRO-7-METHOXY-2*H*-1-BENZAZEPIN-2-ONE WITH EXCELLENT REGIO- AND STEREOSELECTIVITY

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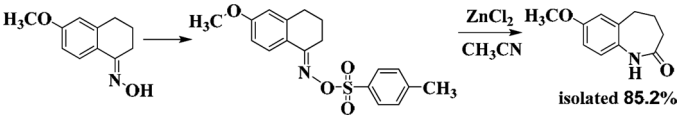
GRAPHICAL ABSTRACT



Abstract *We have surveyed the effects of different acid catalysts, reaction times, and temperatures on the yield, regioselectivity, and stereoselectivity and calculated the ketoxime isomerization and activation energy of the title compound. A facile synthetic procedure with good yields and good regio- and stereoselectivity for Beckmann rearrangement of oxime sulfonate with $ZnCl_2$ in the presence of solvent is developed.*

Keywords Beckmann rearrangement; ketoxime; regio- and stereoselectivity

INTRODUCTION

Both 2,3,4,5-tetrahydro-7-methoxy-1H-2-benzazepin-1-one and 1,3,4,5-tetra hydro-7-methoxy-2H-1-benzazepin-2-one are important organic intermediates in the synthesis of triazolobenzazepine derivatives.[1] These compounds are obtained via either the Beckmann rearrangement of 6-methoxy-3,4-dihydro-naphthalene-1(2H)-one oxime[2–6] or the Schmidt rearrangement of 6-methoxy-3,4-dihydro-naphthalene-1(2H)-one.[7] Beckmann rearrangements usually involve the migration of the groups in the *trans* position to the oxime hydroxyl; however, a mixture of two isomers is obtained when the groups at both ends of the C=N double bond are similar in size.[8]

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6-Methoxy-3,4-dihydronaphthalene-1(2H)-one oxime was synthesized by our group, and the *trans* configuration was determined from its single-crystal structure.[9] According to the mechanism of the Beckmann rearrangement, 6-methoxy-3,4-dihydro-naphthalene-1(2H)-one oxime should produce the title compound. However, because of the similar size of the groups on both ends of the C=N double bond[8] and the electron-donating methoxy group (CH_3O–) in the 6-position of the oxime,[10] the ring expansion of this ketoxime always forms a mixture of the title compound and its isomer in poor yield and requires a time-consuming separation.

To obtain good yields as well as high regio- and stereoselectivies for the rearrangement products, the effect of different acids, solvents, reaction times, and temperatures on these properties were observed. In addition, both the ketoxime isomerization energy and the activation energy of the ring expansion were calculated to determine which conditions resulted in the title compound with the best yield, regio selectivity, and stereoselectivity.

RESULTS AND DISCUSSION

Effects of the Reaction Conditions on the Yield, Regioselectivity and Stereoselectivity of the Rearrangement

At a certain temperature and reaction time in the absence of solvent, both $AlCl_3$[11] and $FeCl_3$[12] catalyze the Beckmann rearrangement to produce the title compound (A) as the primary product along with a small amount of its isomer, 2,3,4,5-tetrahydro-7-methoxy-1H-2-benzazepin-1-one (B). When either CH_3SO_3H[13] or polyphosphoric acid (PPA)[14] are used to catalyze this reaction, the product is a mixture of the two isomers ($A/B \approx 1/2$ based on the spot size ratio of the products on a thin-layer chromatographic, TLC, plate). The effects of the different acids on the yields and both regio- and stereoselectivities of the rearrangement products are shown in Table 1.

An important conclusion can be drawn from these experiments: When Lewis acids, such as $FeCl_3$ and $AlCl_3$, are used to catalyze the Beckmann rearrangement, A is the primary product; however, when Brønsted acids, such as PPA and CH_3SO_3H, are used to catalyze the rearrangement, B is the primary product. The

Table 1. Beckmann rearrangement catalyzed by different acids

						Yield (%)	
Substances	Catalyst	Solvent	Temp. (°C)	Time	A/B[a]	A	B
Oxime	$FeCl_3$	0	80–90	1.5–3 h	4:1[a]	66.3[b]	Trace
	$AlCl_3$	0	150–160	0.5 h	4:1[a]	69.1[b]	Trace
	PPA	0	110–120	25 min	1:2[a]	22.0[c]	45.2[c]
	CH_3SO_3H	0	17	16–18 h	1:2[a]	24.4[b]	47.9[b]
Ketone	CH_3SO_3H, NaN_3	0	6–8	16–18 h	1:2[a]	23.1[b]	47.6[b]

[a]Based on the spot size ratio of the products on a TLC plate.
[b]GC yield.
[c]Isolated yield.

regio- and stereoselectivities of the Beckmann rearrangement catalyzed by $FeCl_3$ and $AlCl_3$ were much greater.

These experiments demonstrated that both time and temperature have a significant impact on the regio- and stereoselectivity of the rearrangement. When anhydrous $FeCl_3$ and ketoxime were ground for 1.5–3 h in a mortar at 80–90 °C, A was the primary product; the proportion of B increased both when the temperature was increased to greater than 90 °C and when the reaction time was extended at 90 °C. However, when the temperature was too high, a by-product was produced, which lowered the yield of B. When the temperature was too low, the reaction either did not occur or only partially occurred. Similar experimental results were obtained using $AlCl_3$ as the catalyst, and the reaction did not occur under 90 °C, occurred only partly from 90–110 °C, and went to completion from 110–125 °C, when PPA was used as the catalyst. The effects of temperature and time on the rearrangement products using an $FeCl_3$ catalyst are shown in Table 2.

It is important to note that, at the beginning of these reactions, only A was produced; however, the content of A decreased and B increased when either the reaction time was extended or the temperature was increased. When the temperature was 90 °C and the reaction time ranged from 1.5 to 3.0 h, the total yield for the two products was maximized. However, when either the reaction time was extended or the temperature was increased, the amount of impurities also increased, and the yield decreased. The same trends were observed for reactions using $AlCl_3$ as the catalyst. Because both of these reactions were conducted in a mortar, a significant amount of product was lost during the reaction workup. In addition, the separation of the isomers was troublesome.

The spot ratio on a TLC of the two products from a Schmidt rearrangement involving a ketone, CH_3SO_3H, and NaN_3 was approximately 1:2 (A/B), with small amounts of other impurities. Both the yield and stereoselectivity were less than those of the Beckmann rearrangement.

Beckmann Rearrangement Mechanism for (1E)-6-Methoxy-3,4-dihydro-naphthalene-1(2h)-one Oxime

To explain these experimental results and obtain both better yields and better regio- and stereoselectivities for the rearrangement products, the mechanism of the Beckmann rearrangement was explored. In the presence of acids, the oxime protonates first and then eliminates one molecule of water to form an electron-deficient nitrogen atom, which is unstable because of its positive charge. The group anti to

Table 2. Effects of temperature and time on the regio- and stereoselectivity of rearrangement catalyzed by $FeCl_3$

		Temp. (90 °C)						Time (3 h)		
Catalyst	Product	20 min	0.5 h	1.5 h	3.5 h	7 h	24 h	90 °C	110 °C	130 °C
$FeCl_3$	A/B[a]	Trace A	9/1	5/1	4/1	2/1	Trace B	4/1	2.5/1	Trace B

[a]Based on the spot size ratio of the products on a TLC plate.

the hydroxyl migrates to the electron-deficient nitrogen atom and promotes the hydrocarbon on the ortho-carbon to complete a 1,2-migration. The formed carbocation reacts with water to produce an amide. This reaction mechanism is shown in Fig. 1.

The direction of the 1,2-migration depends on the stability of the resultant carbocation. Therefore, the aryl group preferentially and selectively migrates to the electron-deficient nitrogen atom, which inserts the nitrogen atom into the ring and forms an aniline-lactam (A). The migration of the alkyl group is a *trans* migration because it can only attack the electron-deficient N atom from the back of the hydroxy group. Therefore, the products obtained are from *trans* migration in most cases. In other words, when the C=N double bond connects to the aryl and alkyl groups at both ends, the aryl group migrates first to yield the corresponding products.[15–17]

When the groups connected to the two ends of the C=N double bond have similar sizes, a mixture of both the aryl and alkyl migration products will be obtained.[8,18] In addition, the electron-donating methoxy group (CH_3O-) in the 6-position of oxime is conducive to alkyl migration.[10] Therefore, this rearrangement produces a mixture of the two isomers.

A *trans* oxime was synthesized by our group,[9] and its isomerization requires a certain amount of energy. When this externally supplied energy is greater than the isomerization energy, the configuration changes.[19] The proposed reaction mechanisms are shown in Figs. 1 and 2.

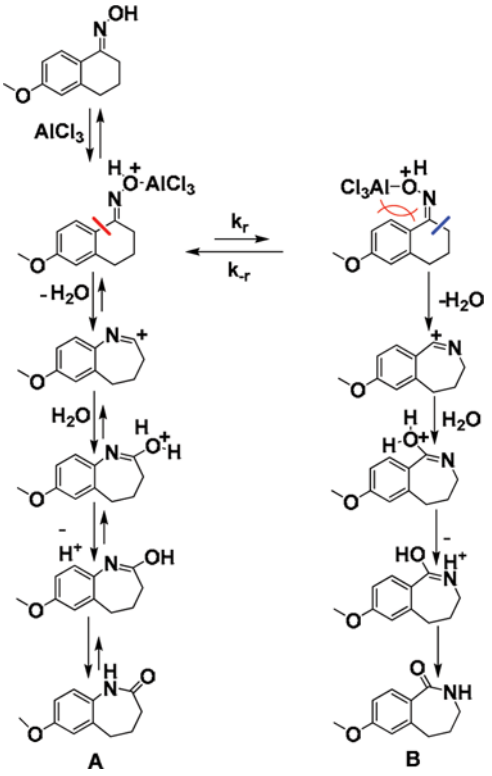


Figure 1. Reaction mechanism. (Figure is provided in color online.)

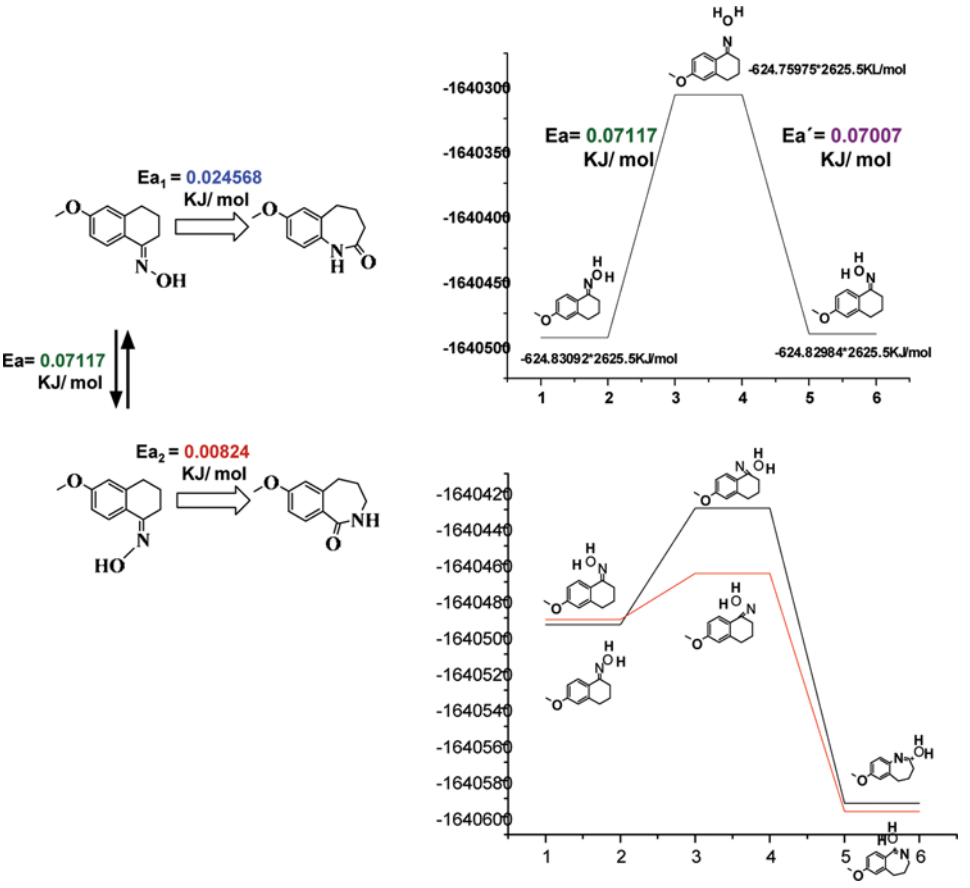


Figure 2. Reaction path. (Figure is provided in color online.)

Based on the experimental results, the ketoxime requires significant energy to isomerize when a Lewis acid, such as $FeCl_3$ or $AlCl_3$, catalyzes the rearrangement. Therefore, the primary product is A. When the temperature is increased to provide more energy, the content of B in the products increases; extending the reaction time also increases the content of B because it is the lower energy and more stable. The energy required for ketoxime isomerization when a Brønsted acid, such as PPA, catalyzes the rearrangement is low. Additionally, B is both lower in energy and more stable than A, and thus, the primary product is B. These results are consistent with the theoretical calculations and reasoning.

According to traditional Beckmann rearrangement theory, the *cis*-ketoxime generates product B, while the *trans*-ketoxime generates A. In this study, the theoretical product should be A because the starting material is purely *trans*-ketoxime. However, product B was obtained because of ketoxime isomerization. During the formation of product A, the alkenyl cation attacks the alkyl cyanide ion; during the formation of product B, the alkyl cation attacks the alkenyl cyanide ion. The alkenyl cation is slightly more stable than the alkyl cation (because of the $\pi-\pi$

conjugation between the C=N and C=C π-orbitals). In addition, the alkyl cation is more stable than a σ-type alkenyl cation. Hence, the intermediate of B is more stable and has lower energy than that of A. Therefore, lower temperatures are conducive to the formation of A, whereas higher temperatures are conducive to the formation of B. Because the formation of A does not require isomerization energy, the reaction rate is much greater; however, increasing the temperature and extending the reaction time increases the formation of product B because of its stability.[20–22]

Calculation of the Ketoxime Isomerization Energy and the Activation Energy of Its Rearrangement

Ab initio calculations were used to obtain the ketoxime isomerization energy and the activation energy of its rearrangement.[23] The obtained results, shown in Fig. 3, were consistent with the expected results. The rate of formation for A was significantly greater than that of B because forming A did not require any isomerization energy and involved a kinetic process. Therefore, A was always produced first during these experiments. Isomerizing the oxime to the *cis* configuration reduces the activation energy required to generate B, which has lower energy and is more stable. Therefore, both increasing the reaction temperature and extending the reaction time increases the ratio of B in the products. This reaction is controlled by thermodynamics. This finding is consistent with those of previous experiments.

Rearrangement of Oxime Sulfonate Catalyzed by $ZnCl_2$

p-Toluenesulfonic acid (PTSA) and $ZnCl_2$ were both added to a solution of ketoxime in acetonitrile. This mixture was refluxed at 90 °C to obtain a mixture of the title compound and its isomer. However, the ketoxime and *p*-toluenesulfonic acid reacted to form the oxime sulfonate, $ZnCl_2$ was then added to the acetonitrile solution, and the mixture was refluxed at 90 °C. The yield of product A was increased to the point that only A was obtained (see Table 3).

This is because the isomerization energy of oxime sulfonate is greater than that of ketoxime. In addition, the Lewis acid catalyst, $ZnCl_2$, further increased the isomerization energy of the rearrangement relative to the Brønsted acid. Therefore,

Table 3. Rearrangement of Oxime in the presence of both acid and PTSA

						Yield (%)	
Substances	Catalyst	Solvent	Temp. (°C)	Time	A/B	A	B
Oxime	PPA/PTSA	0	110–120	25 min	2:1[a]	49.8[b]	24.3[b]
	$ZnCl_2$/PTSA	CH_3CN	Reflux	6 h	2:1[a]	—[d]	—[d]
Oxime sulfonate	PPA	0	110–120	25 min	2:1[a]	54.7[b]	28.6[b]
	$ZnCl_2$	CH_3CN	Reflux	2 h	A	85.2[c]	0

[a]Based on the spot size ratio of the products on a TLC plate.
[b]GC yield.
[c]Isolated yield.
[d]Not tested.

only product A was generated. The product loss of this system is less than that of the solid-phase catalytic rearrangement because of the acetonitrile solvent. The Beckmann rearrangement usually possessed a high conversion yield and selectivity when conducted in the liquid phase.[24–25] This reaction system had a short reaction time, used mild conditions, and resulted in the generation of the product in good yield with good regio- and stereoselectivity.

CONCLUSION

The ring expansion rearrangement of (1E)-6-methoxy-3,4-dihydro-naphthalene-1(2H)-one oxime always produces a mixture of the title compound and its isomer because of the similar sizes of the groups on either end of the C=N double bond and the electron-donating group (CH_3O-) at the 6-position of the oxime. The separation of these two isomers is difficult. The isomerization energy of ketoxime increased significantly when it was converted into oxime sulfonate while using the Lewis acid $ZnCl_2$ to catalyze the Beckmann rearrangement in acetonitrile, which produced only the title compound with good yield.

EXPERIMENTAL

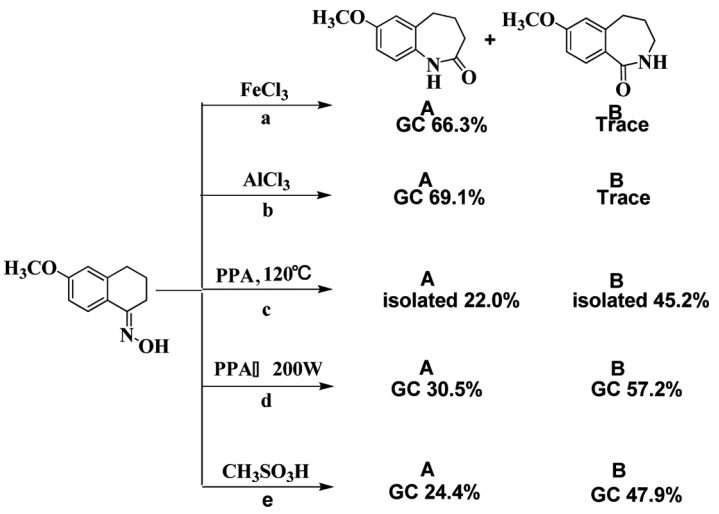
Uncorrected melting points were determined on an X-5 microscope melting point apparatus. Infrared (IR) spectra were recorded (in KBr) on a Fourier transform (FT)–IR (IR Prestige-21). ^{1}H NMR spectra were measured on an AV-300 (Bruker, Switzerland), and all chemical shifts are given in parts per million relative to tetramethylsilane (TMS). Mass spectra were measured on an HP1100LC (Agilent Technologies, USA). Combustion analyses (C, H, and N) were performed on a PE-2400 (Shimadzu). Microanalyses of C, N, and H were performed using a Heraeus CHN rapid analyzer. The major chemicals were purchased from the Alderich Chemical Corporation. All other chemicals were of analytical grade.

Rearrangement of (1E)-6-Methoxy-3,4-dihydro-naphthalene-1(2H)-one Oxime

The Beckmann rearrangements catalyzed by the different acids are shown in Scheme 1. The starting material, (1E)-6-methoxy-3,4-dihydronaphthalen-1(2H)-one oxime,[9] was synthesized using a previously described method.[26] The title compound was prepared from ketoxime using different acids.[11–14] The characterization data for both compounds A and B were consistent with that published in the literature.[27]

Schmidt Rearrangement of (1E)-6-Methoxy-3,4-dihydro-naphthalene-1(2H)-one

The Schmidt rearrangement of the ketone using methane sulfonic acid and sodium azide[7,10,18] is shown in Scheme 2.



Scheme 1. Beckmann rearrangement catalyzed by different acids. Reagents: (a) $FeCl_3$, 80–90 °C, 1.5–3 h; (b) $AlCl_3$, 150–160 °C, 0.5 h; (c) PPA, 120 °C, 25 min; (d) PPA, 200 W, 60 °C, 5–6 h; and (e) CH_3SO_3H, 17 °C, 16–18 h.

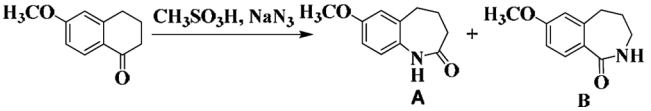
Beckmann Rearrangement of (1E)-6-Methoxy-O-(*p*-toluenesulfonyl)-3,4-dihydro-naphthalene-1(2H)-one Oxime

This ketoxime was converted into an oxime sulfonate,[5] which was in the *trans* configuration according to the single-crystal structure.[28] Afterward, the oxime sulfonate was reacted with PPA and $ZnCl_2$ via the Beckmann rearrangement[29–31] (see Scheme 3).

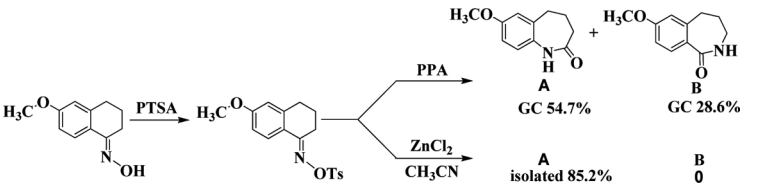
General Methods

The ketoxime (1.0219 g, 5.8 mmol) and *p*-toluenesulfonic acid (1.1148 g, 6.5 mmol) were both dissolved in 10 mL acetone at room temperature, and NaOH (132.6 mg 3.3 mmol) was added. This mixture was stirred for 18 h. After reaching completion, the acetone was evaporated to dryness. The residue was dissolved in ethyl acetate, extracted, and washed three times with water. The organic phase was dried using $MgSO_4$, and the drying reagent was removed via filtration. The ethyl acetate was concentrated via evaporation, and the solution was left overnight to precipitate into colorless crystals with a yield of 95.0%.

Zinc chloride (1.0 mmol) was added to a solution of oxime tosylates (1.0 mmol) in acetonitrile (5 mL). The mixture was heated to reflux (90 °C) for 2 h. The progress



Scheme 2. Schmidt rearrangement of ketone.



Scheme 3. Reaction of oxime tosylate with acid.

of the reaction was monitored by TLC. After the completion of the reaction, the acetonitrile was evaporated, and the residue was dissolved in ethyl acetate and washed with a small amount of water. The combined organic layer was dried over anhydrous magnesium sulfate and filtered. Ethyl acetate was evaporated under reduced pressure to give the crude product, which was recrystallized from ethanol as white crystals, in 85.2% yield.

1,3,4,5-Tetrahydro-7-methoxy-2*H*-1-benzazepin-2-one (A)

Mp 143.9–144.3 °C. IR (KBr), cm^{-1}: 3176, 1676. ^1H NMR ($CDCl_3$, 300 MHz), δ: 2.0–2.3 (m,2H, L -CH_2-), 2.34 (t, $J = 6.9$ Hz, 2H, -CH_2-), 2.77(t, $J = 7.1$ Hz, 2H, -CH_2-), 3.81 (s, 3H, -CH_3), 6.5–7.0 (m, 2H, Ar-H), 6.96 (d, $J = 1.71$ Hz, 1H, Ar-H), 8.27(s, 1H, -NH-). MS (M^+) m/z 191.

2,3,4,5-Tetrahydro-7-methoxy-1*H*-2-benzazepin-1-one (B)

Mp 158.5–159.4 °C. IR (KBr), cm^{-1}: 3186, 1649. ^1H NMR ($CDCl_3$, 300 MHz), δ: 1.9–2.1 (m, 2H, -CH_2-), 2.86 (t, $J = 7.1$ Hz, 2H, -CH_2-), 3.0–3.2 (m, 2H, -CH_2-), 3.86 (s, 3H, -CH_3), 6.65 (s, 1H, -NH-), 6.73 (d, $J = 2.4$ Hz, 1H, Ar-H), 6.86 (dd, $J = 2.4$, 8.5 Hz, 1H, Ar-H), 7.68–7.71 (d, $J = 8.5$ Hz, 1H, Ar-H). MS (M^+) m/z 191.

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