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$Zn(OCOCH_3)_2{\cdot}2H_2O$ Catalysed Efficient Preparation of 2-Phenyl-4-Arylmethylidene-5-Oxazolinones under Ultrasonic Condition

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Abstract

2-Phenyl-4-arylmethylidene-5-oxazolinones were synthesized in very high yield by subjecting a mixture of an aryl aldehyde/heterocyclic aldehyde/cinnamaldehyde and hippuric acid in anhydrous acetic anhydride and catalytic $Zn(OCOCH_3)_2{\cdot}2H_2O$ to ultrasonication at 35 KHz for 4 to 8 min. This method has many advantages: use of a green catalyst; yields are high, involves easy workup procedure, is energy efficient and economically feasible.

Keywords

2-phenyl-4-arylmethylidene-5-oxazolinones; $Zn(OCOCH_3)_2{\bullet}2H_2O$; hippuric acid; araldehydes; acetic anhydride; ultrasonication

1. Introduction

2-Phenyl-4-aryl methylidene-5-oxazolinones are important in synthesizing fine chemicals and serve as precursors for biologically active molecules such as: unsaturated amino acids, peptides and biosensors [1]. Oxazolin-5-ones are multifunctional due to the presence of C=C, C=N, and C=O bonds. Hence, they are important in the synthesis of natural products and pharmaceutical chemicals [2, 3].

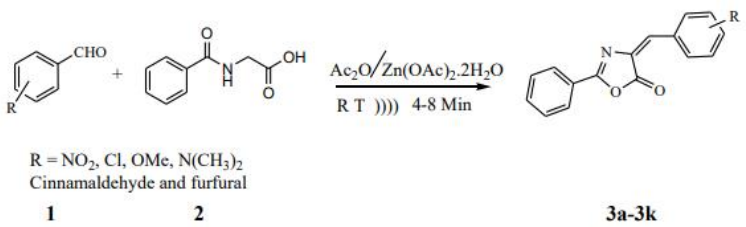
Substituted oxazoles are important as they are compatible in the preparation of biologically active molecules such as: anti-bacterial, antifungal, anti-inflammatory [2-4], analgesic [5], anticancer [6, 7], anti-diabetic [8] and antiobesity [9] agents. Further, 2-phenyl-4-aryl methylidene-5-oxazolinones are useful for the synthesis of thiadiazoles and triazoles [10] which also exhibit antimycobacterial [11, 12], antimycotic [13] and antidepressive [14] activities. Oxazoles are further used as fluorescent whitening agents, dyes, pigments and lubricants [15-18].

The development of methods for azlactones is still an active field of investigation. Erlenmeyer Plöchl's reaction of an aldehyde, hippuric acid in acetic anhydride by using sodium acetate as a catalyst is well known [19]. Erlenmeyer Plöchl reaction has remained unchanged since the last century with some modification of catalysts such as: zwitter ionic imidazolium salt [20], [$Yb(OTf)_3$] [21], [TCT,PPh_3] [22], [TsCl/DMF] [23], nano-sphere SiO_2–AP [24], AcOK [25], Montmorillonite K-10 [26], MgO/Al_2O_3 [27], KF-Al_2O_3 [28], silica–alumina supported heteropolyacids [29], Nano Fe_2O_3 [30], $Ca(OAc)_2$ [31], Bi(III) Salts [32], [CellFemImi]OH [33], $[bmim]_3PW_{12}O_{40}$ [34], $[bmim]PF_6$ or $[bmim]BF_4$ [35]. However, some of these methods have their excellence, but, suffer from drawbacks such as: high temperature, low yields, generation of toxic substances, and use of stoichiometric catalysts.

Sonochemistry has received attention in the past two decades. The driving force of ultrasonic reactions has many facets: The method is energy efficient, hence, is economical, the reactions can be scaled up using ultrasonic reactors; there is a need for a technology that minimizes the waste [36].

2. Results & Discussion

In continuation of our work on the preparation of oxazolin-5-ones using iodine as a catalyst under microwave irradiation [37], and the use of nano MgO under sonic condition [38], which have got their own advantages; and in continuation of our work on ultrasound-assisted reactions [39-47] we, herein, report another energy efficient synthesis of oxazolin-5-ones from hippuric acid, aryl aldehydes/heterocyclic aldehyde (furfural)/cinnamaldehyde and acetic anhydride in the presence of readily available, green and highly economical catalyst $Zn(OCOCH_3)_2{\cdot}2H_2O$ under the sonic condition as shown in the Scheme1.



Scheme1 Preparation of 2-phenyl-4-substitutedmethylidene-5-oxazolinones using catalytic $Zn(OCOCH_3)_2{\cdot}2H_2O$ under sonic condition.

To evaluate the suitability of $Zn(OCOCH_3)_2{\cdot}2H_2O$, and to establish its catalytic role in the synthesis of biologically important oxazoline-5-ones, we initiated the present study at room temperature using hippuric acid, aryl aldehydes/heterocyclic aldehyde/cinnamaldehyde and acetic anhydride in EtOH as a solvent.

Several catalysts were examined for oxazoline-5-ones synthesis; to find the correct condition, a control reaction was carried out without a catalyst to get 5% product as presented in Table 1 (entry 1). Furthermore, to optimize the reaction conditions, we executed the reaction of 4-chlorobenzaldehyde with hippuric acid in acetic anhydride and $Zn(OCOCH_3)_2{\cdot}2H_2O$ as an activator under diverse reaction environments such as: mechanical stirring, grinding, heating, refluxing in Ethanol, and under sonic condition. Grinding of the reactants with $Zn(OCOCH_3)_2{\cdot}2H_2O$ gave a low yield (entry 14). On further investigation, we found that, the product yield is low under different conditions. Delightfully, $Zn(OCOCH_3)_2{\cdot}2H_2O$ efficiently promoted the transformation under ultrasonic condition showing the highest degree of conversion, as it gave a very high yield in a short time (Table 1, entry 16). When the reaction was carried out under ultrasonication, the product was obtained in 95% yield within 8 min. The obtained results have been compared with some of the available methods in the literature for the preparation of 5-oxazolinones and the details are presented in Table 1.

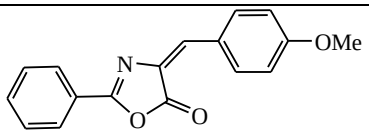
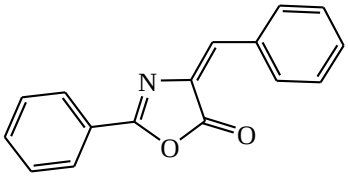
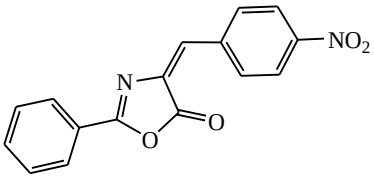
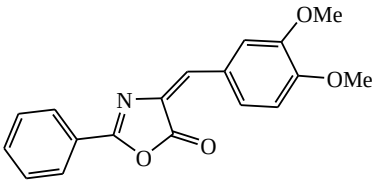
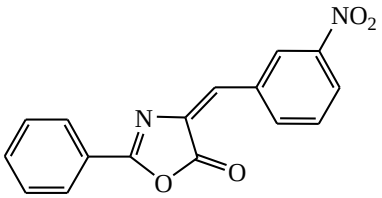
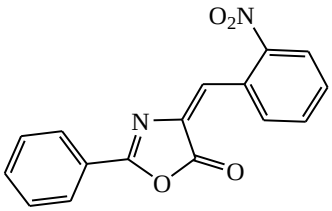
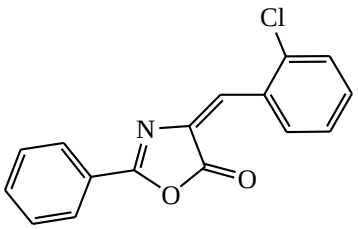
Table 1 Synthesis of 2-Phenyl-4-(4'-chlorophenylmethylidene)-5-oxazolinone under varied conditions.

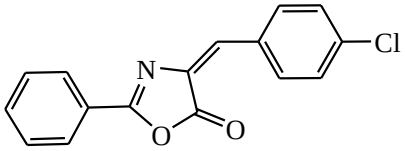
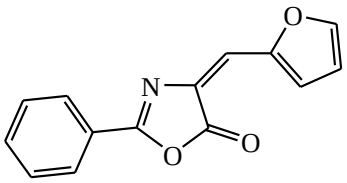
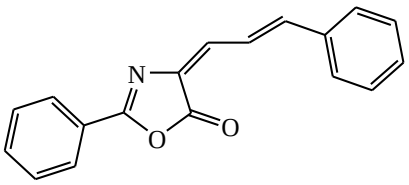
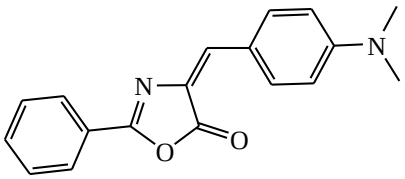
Entry	Catalyst	Reaction condition	Solvent& Temp(°C)	Time (min)	Yield (%)
01	No catalyst	)))))	Ethanol, RT	60	5
02	Imidazolium salt	Stirring	No-Solvent, 60	240	76 [20]
03	TCT, PPh_3, base	Grinding	THF, RT	-	80 [22]
04	$Yb(OTf)_3$, Ac_2O	Stirring	No-Solvent, 40	1-5	80 [21]
05	AcOK, Ac_2O	Reflux	No-Solvent	15	83 [25]
06	Montmorillonite K-10, Ac_2O	Reflux	EtoAc	240	84[26]
07	TiO_2 NPs	Stirring	Ethanol, 120	30	93 [2]
08	AcONa	Stirring	No-Solvent, 60	180	65 [1]
09	MgO/ Al_2O_3, Ac_2O	MW	No-Solvent	6-10	85 [27]
10	TsCl/DMF	MW	No-Solvent, (450W)	150	88 [23]
11	KF-Al_2O_3, Ac_2O	Stirring	No-Solvent, 60	60	89 [28]
12	Nano-SiO_2–AP	MW	No-Solvent	180	93 [24]
13	$Zn(OCOCH_3)_2{\cdot}2H_2O$	Reflux	Ethanol, RT	90	70
14	$Zn(OCOCH_3)_2{\cdot}2H_2O$	Grinding	No-Solvent	10	10
15	$Zn(OCOCH_3)_2{\cdot}2H_2O$	Stirring	Ethanol, RT	240	50
16	$Zn(OCOCH_3)_2{\cdot}2H_2O$	)))))	Ethanol, RT	08	95

After examining the various reaction parameters, we examined the substrate scope and efficiency of the reaction with aryl/het(aryl)/cinnamyl aldehydes having electron withdrawing and electron donating groups in their aromatic rings, to get the corresponding products in very good to

high yields under optimized reaction conditions as shown in Table 2. The ^{1}HNMR spectra of all the prepared 5-oxazolinones showed characteristic methylidene proton signal between δ 7.22 and 8.37 ppm. The azalactone carbonyl group showed a strong signal in the IR spectra between υ 1797 to 1785 cm^{-1} of all the prepared products.

Table 2 Conversion of aryl aldehydes/furfural/cinnamaldehyde into the corresponding 2-phenyl-4-substitutedmethylidene-5-oxazolinones using catalytic $Zn(OCOCH_3)_2{\cdot}2H_2O$ under sonic condition.

Entry	Product	ν C=O (cm^{-1})	Yield[a] (%)	Time (min)	Melting point (°C) Observed Reported
3a		1787.89	96	5	164 164-165 [31]
3b		1793.68	91	6	169 169-170 [2]
3c		1797.53	94	8	240 242-243 [2]
3d		1785.96	96	5	140 150-152 [31]
3e		1789.82	92	8	194 194-195 [31]
3f		1793.65	91	7	165 164-165 [31]
3g		1793.86	94	6	138-140 159-160 [28]

3h		1795.60	95	4	205 203-204 [31]
3i		1789.82	93	5	169-170 169-170 [2]
3j		1785.96	94	5	130 128-129 [2]
3k		1787.67	91	7	212 211-213 [20]

[a] Isolated yield.

3. Methods

3.1 Materials and Instruments

$Zn(OCOCH_3)_2 \cdot 2H_2O$, acetic anhydride, aryl aldehydes/furfural/cinnamaldehyde, hippuric acid and other chemicals are commercial. Silica gel G254 TLC regulated the reactions under a UV lamp. The reactions were studied in a sonic bath at 35 kHz at 25°C. The IR spectra were recorded using a SHIMADZU FT-IR-8400S instrument, and ^{1}HNMR spectra on a 400 MHz Bruker spectrophotometer in $CDCl_3$ as a solvent.

3.2 General Procedure

Two mmol each of aryl aldehyde/furfural/ cinnamaldehyde, hippuric acid, 4 mmol of acetic anhydride and 0.5 mmol $Zn(OCOCH_3)_2 \cdot 2H_2O$ in 3 mL ethanol were integrated well, and shrilled in the sonic bath for 4–8 min (Table 2). The crude product was filtered, washed with hot water and recrystallized from methanol-water (2:1) to get 90–95% product.

3.3 Spectral Data

3.3.1 2-Phenyl-4-(4'-Methoxyphenylmethylidene)-5-Oxazolinone (3a): [48]

IR (KBr): ν C=O 1787.89 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.87 (s, 3H), 6.95–6.99 (d, 2H, *J* = 8.8 Hz), 7.26 (s, 1H, =C-H), 7.43–7.57 (m, 3H), 8.18–8.19 (m, 2H), 8.21 (d, 2H, *J* = 8.8 Hz) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 55.56, 113.74, 114.53, 127.06, 128.1, 128.8, 131.8, 132.31, 134.58, 162.2, 167.9 ppm.

3.3.2 2-Phenyl-4-Benzylidene-5-Oxazolinone (3b): [48]

IR (KBr): ν C=O 1790 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (s, 1H, =C-H), 7.46–7.64 (m, 5H, ArH), 8.18–8.23 (m, 5H, ArH) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ125.63, 128.40, 128.91, 131.20, 131.80, 132.47, 133.36, 133.55 ppm.

3.3.3 4-(4'-Nitropheylmethylidene)-5-Oxazolinone (3c): [49]

IR (KBr): ν C=O 1785.53 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (s, 1H, =C-H), 7.62–8.05 (m, 5H, ArH), 7.96 (dd, 2H, H-2′ and H-6′), 8.20 (dd, 2H, H-3′ and H-5′) ppm.

^{13}C NMR (100 MHz, CDCl3): δ 118.5, 126.9, 128.3, 129.2, 131.1, 132.4, 134.8, 138.2, 142.6, 147.5, 161.7, 173.2 ppm

MS (ESI) m/z: 294.06 $[M+H]^{+\bullet}$.

3.3.4 2-Phenyl-4-(3′,4′-Dimethoxyphenylmethylidene)-5-Oxazolinone (3d):

IR (KBr): ν C=O 1785.96 cm^{-1}.

^{1}HMR (400 MHz, $CDCl_3$): δ 3.98 (s, 3H), 4.04 (s, 3H), 6.95 (d, 1H, *J* = 9 .2) 7.22 (s, 1H, =C-H), 7.55 (m, 4H, *J* = 8.4 Hz), 8.15 (s, 1H), 8.19 (d, 2H, *J* = 9.6 Hz) ppm.

^{13}C NMR (100 MHz, CDCl3): δ 110.91, 113.98, 126.88, 127.96, 128.05, 128.97, 131.21, 132.10, 133.06, 149.22, 152.10, 162.48, 167.84 ppm.

3.3.5 2-Phenyl-4-(3'-Nitrophenylmethyidene)-5-Oxazolinone (3e): [49]

IR (KBr): ν C=O 1787.89 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (s, 1H, =C-H), 7.50–7.95 (m, 5H, ArH), 7.62 (t, 1H, H-5′), 7.84 (dd, 1H, H-6′), 8.19 (dd, 1H, H-4′), 8.54 (s, 1H, H-2′) ppm.

^{13}C NMR (100 MHz, CDCl3): δ 121.7, 125.4, 127.6, 128.8, 129.1, 129.9, 131.8, 132.8, 134.3, 135.1, 141.8, 148.5, 160.9, 171.5 ppm.

MS (ESI) m/z: 294.06 $[M+H]^{+\bullet}$.

3.3.6 2-Phenyl-4-(2'-Nitrophenylmethylidene)-5-Oxazolinone (3f): [50]

IR (KBr): ν C=O 1793.68 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53–7.96 (m, 5H, Ar-H), 7.80–8.01 (m, 4H, Ar-H), 8.37 (s, 1H, =C-H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 112.2, 123.2, 126.1, 127.1, 127.3, 128.0, 128.4, 128.5, 128.7, 128.9, 131.0, 131.1, 134.2, 147.3, 160.8, 165.9 ppm.

MS (ESI) m/z: 295.06 [M+H]; HRMS-EI: found: 294.064, calculated: 294.071.

3.3.7 2-Phenyl-4-(2'-Chlorophenylmethylidene)-5-Oxazolinone (3g): [50]

IR (KBr): ν C=O 1793.68 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51–7.94 (m, 5H, Ar-H), 7.31–7.43 (m, 4H, Ar-H), 7.63 (s, 1H, C=C-H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 112.3, 126.0, 126.3, 127.3, 128.0, 128.3, 128.5, 128.8, 131.1, 131.3,

132.3, 133.5, 160.1, 168.9 ppm.
MS (ESI) m/z: 284.04 [M+H];
HRMS-EI: found: 283.040, calculated: 283.047.

3.3.8 2-Phenyl-4-(4'-Chlorophenylmethylidene)-5-Oxazolinone (3h):

IR (KBr): ν C=O 1795.6 cm^{-1}.
^{1}HMR (400 MHz, $CDCl_3$): δ 7.37 (s, 1H, =C-H), 7.59–7.73 (m, 5H), 8.12 (d, 2H, *J* = 7.2 Hz), 8.31 (d, 2H, *J* = 8.2 Hz) ppm.

3.3.9 2-Phenyl-4-(2'-Furylmethylidene)-5-Oxazolinone (3i):

IR (KBr): ν C=O 1789.82 cm^{-1}.
^{1}HMR (400 MHz, $CDCl_3$): δ 6.83 (d, 1H, *J* = 3.6 Hz), 7.27 (s, 1H, =C-H), 7.60–7.62 (m, 3H), 7.68 (d, 1H, *J* = 7.2 Hz), 8.08–8.11 (m, 3H) ppm.

3.3.10 2-Phenyl-4-(*E*-Styrylmethylidene)-5-Oxazolinone (3j):

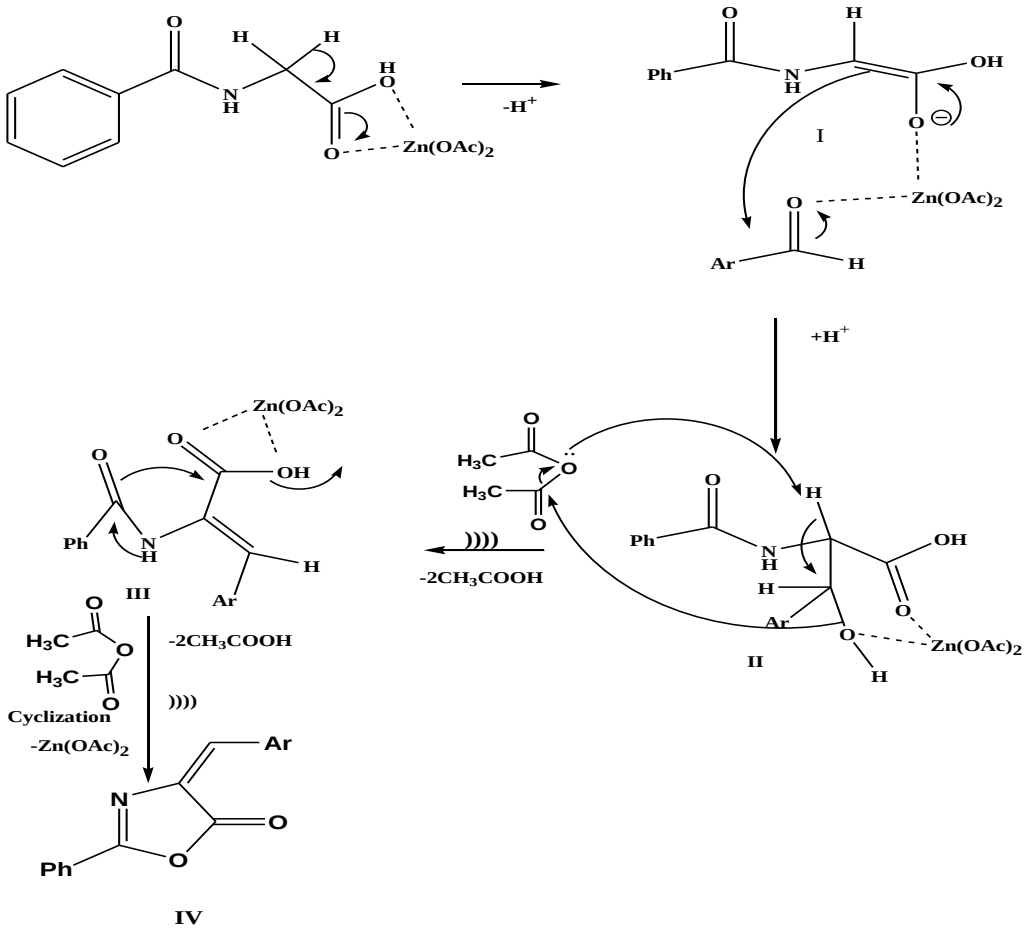
IR (KBr): ν C=O 1785.96 cm^{-1}.
^{1}HMR (400 MHz, $CDCl_3$): δ 6.709 (d, 2H, *J* = 12 Hz), 7.23 (d, 1H, *J* = 7.6 Hz, =C-H), 7.52–7.61 (m, 5H), 8.23–8.27 (m, 5H) ppm.

3.3.11 2-Phenyl-4-(4'-*N*,*N*-Dimethylaminophenylmethylidene)-5-Oxazolinone (3k): [49]

IR (KBr): ν C=O 1787.89 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.98 (s, 6H, 2 × CH3), 6.64 (dd, 2H), 7.18 (dd, 2H), 7.36 (s, 1H, =C-H), 7.60–8.10 (m, 5H, ArH) ppm.
^{13}C NMR (100 MHz, $CDCl_3$): δ 44.1, 113.2, 126.8, 128.1, 128.9, 129.8, 131.2, 132.4, 134.8, 141.6, 151.7, 163.8, 175.3 ppm.
MS (ESI) m/z: 292.12 $[M+H]^{+\bullet}$.

4. Mechanism

In the present reaction, hippuric acid gets activated by Zn $(OCOCH_3)_2$ followed by conjugate addition of **I** across the carbonyl carbon of the aldehyde takes place to give intermediate **II**, which reacts with a molecule of acetic anhydride and loses two molecules of acetic acid to give the intermediate **III**. In the final step the loss of two more molecules of acetic acid from **III** in the presence of another molecule of acetic anhydride may occur to give the product **IV**. The last two steps are important, and we feel that, ultrasound is responsible for enhancing the rate as shown in the Scheme 2.



Scheme 2 Mechanism of formation of 2-phenyl-4-arylmethylidene-5-oxazolinones.

5. Conclusion

In conclusion, an ultrasound-assisted, highly economical, energy-efficient method for the preparation of biologically important oxazoline-5-one derivatives by the condensation of hippuric acid with aryl aldehydes/furfural/cinnamaldehyde in acetic anhydride/EtOH and $Zn(OCOCH_3)_2{\cdot}2H_2O$ as a catalyst has been developed. The present method is efficient and simple, high yield, short duration and ease of workup make the method advantageous. Most importantly, the crude product quality is high enough that, in some cases, further purification is not required.

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Author Contributions

Dr. Sadeq Hamood Saled Azzam prepared the oxazoline-5-ones and characterized them and prepared the draft of the manuscript. Ms. Amreen Khanum repeated the synthesis of oxazoline-5-ones as per the reviewers suggestions, characterized them and updated the references. Prof.

Mohamed Afzal Pasha is the corresponding author, Research supervisor, corrected and edited the manuscript and Guided both the coauthors.

Competing Interests

The authors have declared that no competing interests exist.

Additional Materials

The following additional materials are uploaded at the page of this paper.

1. Supplementary.

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