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Synthesis of Some New Functionalized Quinoxaline Derivatives Using Choline Chloride: 2 $ZnCl_2$ as a Reusable Catalyst

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Abstract

A novel and simple way to synthesize quinoxaline derivatives bearing functional group moieties in a one-pot reaction from o-phenylenediamine and benzil derivatives in the presence of Choline chloride:2 $ZnCl_2$ as a green and reusable catalyst is described. The products were characterized by using FT-IR, ^{1}H-NMR, ^{13}C-NMR, and comparing the melting points with authentic samples. The reaction was followed by the nucleophilic addition mechanism in which the catalyst polarizes, and promotes the carbonyl groups. The catalyst used was presented with several advantages, including easy preparation, low price, high stability, proper reusability, easy separation, purification from the reaction mixture, and an outstanding yield of quinoxaline derivatives under a suitable temperature and reaction time in a non-toxic solvent.

Keywords: Deep-Eutectic Solvent, quinoxaline, Benzil, Functional groups.

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Introduction

The synthesis of quinoxalines and their derivatives has received significant attention due to their various biological activities, such as antibacterial and anti-tumor [1, 2] , antiviral [3], anti-depression [4], anthelmintic [5], antituberculosis [6], antiprotozoal [7], and anti-inflammatory activities [8]. Besides, these compounds are utilized in different industries due to their ability to prevent metal corrosion [9], and their applicability for preparing, polymers with excellent thermal stability [10], electroluminescent materials [11], agrochemicals [12] and other compounds with wide-spectrum applications [13]. These materials are generally synthesized through various procedures and are rarely found naturally [14]. Numerous methods have been developed to synthesize quinoxaline derivatives, such as the condensation of 1,2-diamines with α-diketones [15] , 1,4-addition of 1,2-diamines to diazenylbutenes [16] , cyclization-oxidation of phenacyl bromides [17], and oxidative coupling of epoxides with ene-1,2-diamines [18].

More recently, several strategies have been reported to prepare quinoxaline derivatives, enhance reaction efficiency, reduce reaction time and increase catalyst stability, such as microwave-assisted synthesis, using recyclable catalysts, synthesis in aqueous media [19], synthesis under ultrasound irradiation at room temperature [20], and sonication-based reactions [21]. The most common synthetic approach for preparing quinoxaline derivatives involves one-pot condensation of *o*-phenylenediamines and 1,2-diketone derivatives in the presence of a suitable and acidic catalyst [13]. In this procedure, the catalyst plays an essential role in the synthesis of quinoxaline derivatives.

Various heterogeneous catalysts, such as bentonite clay K-10 [22], phosphate-based heterogeneous catalyst [23], Fe catalysis [24], Zirconium (IV) modified silicagel [25], cellulose sulfuric acid [26] and $Ga(OTf)_3$ [27], have already been applied to prepare quinoxaline derivatives. Although these catalysts have yielded high outputs of quinoxaline derivatives, the synthesis of these catalysts involves several steps, requires many reactants, and usually takes a long time [28]. Therefore, novel, inexpensive, and environmentally-friendly catalysts with rather few reaction steps, requiring low amounts of reagents, low synthesis time, and high reusability are required for the synthesis of quinoxaline derivatives. Room-temperature ionic liquids (RTILs), as green solvents, have various applications in different chemical procedures due to their low volatility, proper viscosity, meager vapor pressure, and being liquid at room temperature [29].

Deep eutectic solvents (DESs), promising class of RTILs, are used in synthetic reactions as a material with a dual role, both as a solvent and a catalyst. Due to a simple synthesis process, low price, excellent biosafety, and biodegradability as well as other appropriate properties of

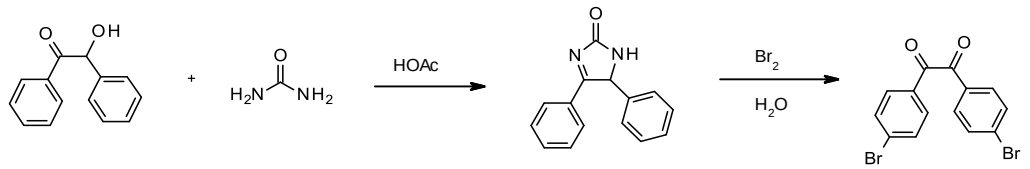
ionic liquids, DESs provide a perfect choice to obviate some of the limitations of RTILs [30]. DESs are prepared by mixing two or more components, which can be accomplished by forming hydrogen bonds. In this process, a hydrogen bond acceptor is combined with a hydrogen bond donor to prepare a eutectic mixture, where the melting point of the prepared DES is lower than the melting point of its components [31]. According to these findings and regarding the valuable properties of quinoxaline derivatives [13], we here aimed to present an efficient approach using a DES-based on choline chloride-$ZnCl_2$ with a molar ratio of 1:2, as a green and reusable catalyst and solvent under a one-pot reaction to prepare some new quinoxalines containing various functional groups.

Experimental

All the chemicals were purchased from Merck (Germany). 4,4′-dibromobenzil and 3,3′-dinitrobenzil were prepared as mentioned previously with some modifications [32, 33]. ChCl: 2 $ZnCl_2$ was prepared according to the reported procedures [34]. Melting points were obtained in open capillary tubes and were measured by an Electrothermal 9100 apparatus. FT-IR spectra were recorded using a Bruker Tensor 27 spectrometer using KBr pellets. ^1H and ^{13}C NMR spectra were determined on a Bruker 300 DRX Avance instrument using DMSO-d_6 as solvent and tetramethyl silane as an internal standard. The mass spectra were scanned on an Agilent Technologies instrument at 70 eV. Elemental analysis was performed by a Thermo Finnigan Flash EA microanalyzer.

Synthesis of 4,4′-dibromobenzil

4,4′-dibromobenzil was prepared based on, a two-steps reaction by the condensation of benzoin with urea, followed by bromination and hydrolysis, as described earlier [32].



Scheme 1. Synthesis of 4,4′-dibromobenzil.

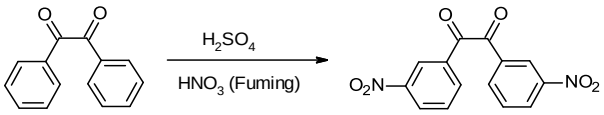
Synthesis of 3,3′-dinitrobenzil

3,3′-Dinitrobenzil was prepared according to the literature procedure (Scheme 2) [33]. Briefly, concentrated sulfuric acid (100.0 mL, 183.17 gr, 1.86 mol) and benzil (21.0 gr, 0.1 mol) were

mixed in a 500 mL round-bottom flask under stirring while cooled in a salt/ice bath. Fuming nitric acid (12.5 mL, 0.3 mol) was added dropwise from a funnel under stirring for 60 min., and controlling the reaction's temperature in the range of -7.5 ± 2.5 ^{o} C. The color of the reaction mixture gradually turned into light yellow. The mixture was stirred overnight at ambient temperature, followed by adding a large volume of ice-distilled water (100 gr:1 liter) to the mixture. Then, the mixture was filtered through a Büchner funnel, washed with ethanol, recrystallized with acetic acid (150 mL), and dried in air. Light yellow needles; yield. 24.4 g (88 %); m.p. 130-132 °C.

^{1}H NMR (DMSO-*d6*) δ: 7.92 (t, *J* = 8.1 Hz, 1H, Ar H), 8.44–8.47 (m, 1H, Ar H) 8.57–8.61 (m, 1H, Ar H), 8.77 (t, *J* = 2.1 Hz, 1H, Ar H);

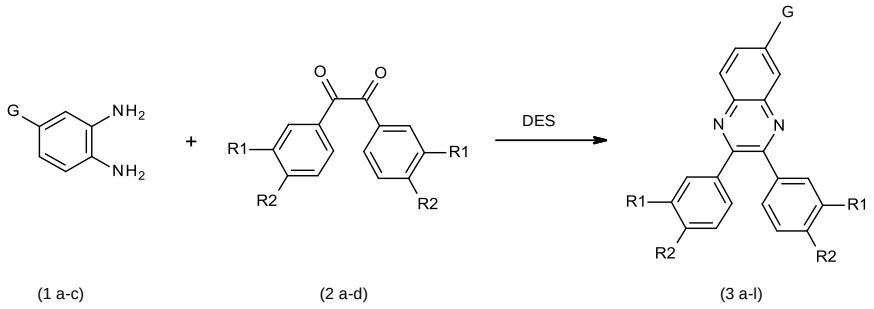
^{13}CNMR(DMSO-d6,400MHz)δ(ppm): 124.01, 124.95, 129.59, 131.38, 135.67, 140.02, 141.48, 148.44, 150.24.



Scheme 2. **Synthesis of 3,3′-dinitrobenzil.**

Typical procedure for synthesis of quinoxaline derivatives

A mixture of *o*-phenylenediamine derivative (20 mmol), benzil derivative (20 mmol) and choline chloride:2 $ZnCl_2$ (0.8 gr) was heated on an oil bath at 120 °C for 10 min. Then, the reaction mixture was cooled to room temperature, cold ethanol was then added to the mixture and the precipitate was filtered off, washed with ethanol, and dried. The filtrate was collected for the separation and reusing of the catalyst.



Scheme 3. Synthesis of quinoxaline derivatives.

Reusability of the catalyst

The catalyst (choline chloride:2 $ZnCl_2$) was soluble in ethanol, rendering it retrievable from the reaction mixture. Then the catalyst was washed with diethyl ether, dried in the vacuum

oven at 50 °C for 2 h, and reused in another reaction. The recycled catalyst was reused in four additional reactions without any evidence for appreciable degeneration of its catalytic activity.

The selected spectral data

2,3-bis(3-nitrophenyl)quinoxaline (3d): White solid, yield 0.35 g, 94%, FT-IR (KBr) (ν_{max}/ cm^{-1}): 1528 and 1490 (NO_2), 1000-1400(C=C,C=N); ^{1}H NMR (DMSO-d_6, δ, ppm): 7.57 (t, *J* = 7.8 Hz, 2H, Ar H), 7.81 (d, *J* = 7.8 Hz, 2H, Ar H), 7.92–7.95 (m, 2H, Ar H), 8.25-8.32 (m, 4H, Ar H), 8.57 (t, *J* = 1.8 Hz, 2H, Ar H); ^{13}C NMR (DMSO-d_6, δ, ppm): 124.1, 124.9, 129.6, 131.4, 135.7, 140.0, 141.5, 148.4, 150.2. Elemental Analysis for $C_{20}H_{12}N_4O_4$: C 64·52, H 3·25, N 15.05%. Found: C 64.38, H 3.37, N 14.94%; MS (m/z): 372.

6-nitro-2,3-bis(3-nitrophenyl) quinoxaline (3e): Cream solid, yield 0.36 g, 96%, IR (KBr) (νmax/ cm-1): 3083 (=CH),1522 and 1479 (NO_2), 1000-1400(C=C, C=N). ^{1}H NMR (DMSO-d_6, δ, ppm): 7.69 (t, J = 7.8 Hz, 2H, Ar H), 7.58 (d, J = 8.69 Hz, 4H, Ar H), 8.48-8.51 (m, 5H, Ar H), 9.02 (d, J = 7.3 Hz, 1H, Ar H); ^{13}C NMR (DMSO-d_6, δ, ppm):124.2, 125.1, 129.6, 130.3, 132.1, 133.6, 135.67, 139.1, 140.5, 146.5, 148.8, 150.6, 151.2, 151.8, 155.7, 156.8. Elemental Analysis for $C_{20}H_{11}N_5O_6$: C 57.56, H 2.66, N 16·78%. Found: C 57.25, H 2.38, N 17.08%; MS (m/z): 417.

6-methyl-2,3-bis (3-nitrophenyl)quinoxaline (3f): Cream solid, yield 0.33 g, 95%, IR (KBr) (ν_{max}/ cm^{-1}): 2916 (CH_3), 1518 and 1478 (NO_2), 1000-1400(C=C,C=N); ^{1}H NMR (DMSO-d_6, δ, ppm): 1.96 (s, 3H, CH_3), 7.69 (t, *J* = 7.8 Hz, 2H, Ar H), 7.92 (d, *J* = 7.8 Hz, 2H, Ar H), 8.33 (d-d, *J* =5.7 and 2.4 Hz, 2H, Ar H), 8.48-8.51 (m, 3H, Ar H), 8.66 (d, *J* =6.6 Hz, 1H, Ar H), 9.05 (d, *J* = 2.4 Hz, 1H, Ar H)); ^{13}C NMR (DMSO-d_6, δ, ppm): 29.7,76.6, 77.0, 77.4, 124, 124.9, 129.9, 131.2, 135/6, 140, 141.4,148.4,150.2. Elemental Analysis for $C_{21}H_{14}N_4O_4$: C 65.28, H 3.65, N 14.50%. Found: C 65.82, H 3.70, N 14.48%; MS (m/z): 386.

2,3-bis (4-bromophenyl)-6-nitroquinoxaline(3h): Cream solid, yield 0.33 g, 90%, IR (KBr) (ν_{max}/ cm^{-1}): 3090 (=CH), 1526 or 1487 (NO_2), 1000-1400 (C=C,C=N); ^{1}H NMR (DMSO-d_6, δ, ppm):7.48 (d-d, *J* =5.4 and 3.0 Hz, 4H, Ar H), 7.59 (d, *J* = 8.4 Hz, 4H, Ar H), 8.32 (d, *J* = 9.3 Hz, 1H, Ar H), 8.58 (d-d, *J* =6.9 and 2.4 Hz, 1H, Ar H), 9.10 (s, 1H, Ar H); ^{13}C NMR (DMSO-d_6, δ, ppm):123.7, 124.7, 124.8, 125.6, 130.8, 131.4, 131.5, 131.9, 136.6, 136.7, 139.9, 431.5, 148.1, 154.1, 154.8. Elemental Analysis for $C_{20}H_{11}Br_2N_3O_2$: C 49.52, H 2.29, N 8.66 %. Found: C 50.49, H 2.40, N 8.73%; MS (m/z): 484.92.

Results and discussion

Catalysts and solvents play a critical role in the synthesis of organic compounds. For this purpose, it is essential for solvents/catalysts to have little prices, great solute solubility, low toxicity, and environmental compatibility. In this study, a model reaction (synthesis of 2,3-diphenyl quinoxaline (**3a**)) was initially carried out to determine the optimum reaction conditions and evaluate the catalytic efficiency, in various protic and aprotic solvents such as EtOH, HOAc, Toluene, CH_3CN, DMF, and DMSO, as well as under solvent free-condition (Table 1).

Table 1. Reaction of o-phenylenediamine (0.1 mol) with benzil (0.1 mol) at different condition.

Entry	Solvent (mL)	Catalyst (mol%)	Temperature (°C)	Time (min.)	Yield (%)
1	HOAc (10)	ChCl: $ZnCl_2$ (5)	100	10	75
2	HOAc (10)	ChCl: 2 $ZnCl_2$ (5)	100	10	85
3	HOAc (10)	ChCl: 2 $ZnCl_2$ (10)	100	10	90
4	HOAc (10)	ChCl: 2 $ZnCl_2$ (15)	100	10	90
5	HOAc (10)	ChCl: 2 $ZnCl_2$ (10)	120	10	98
6	EtOH (10)	ChCl: 2 $ZnCl_2$ (10)	60	15	63
7	Toluene (10)	ChCl: 2 $ZnCl_2$ (10)	60	15	55
8	CH_3CN (10)	ChCl: 2 $ZnCl_2$ (10)	60	15	66
9	DMF (10)	ChCl: 2 $ZnCl_2$ (10)	100	10	68
10	DMSO (10)	ChCl: 2 $ZnCl_2$ (10)	100	10	75
11	-	ChCl: 2 $ZnCl_2$ (5)	120	20	70
12	-	ChCl: 2 $ZnCl_2$ (10)	90	15	85
13	-	ChCl: 2 $ZnCl_2$ (10)	100	10	90
14	-	ChCl: 2 $ZnCl_2$ (10)	120	10	98
15	-	ChCl: 2 $ZnCl_2$ (15)	120	10	98

The results indicated a high yield (98 %) in solvent-free conditions in the presence of ChCl: $ZnCl_2$ at 120 ^oC and a reaction time of 10 min. Under solvent-free conditions Besides, the impact of temperature on the reaction yield is greater than the effect of reaction time, indicating that the thermodynamics of the reaction is more effective than its kinetics (Table 1, entries 13 and 14). Adding solvents such as EtOH, Toluene, CH_3CN, DMF, and DMSO reduced the yield compared to solvent-free conditions. However, an increase in the yield was observed upon using polar solvents. The lowest yield was obtained when using 10 mL of Toluene as a solvent with the lowest polarity for 15 min at 60 ^oC (Table 1, entry 7). Reactions in the EtOH, toluene,

and CH_3CN solvents (for 15 min) yielded low amounts of products (Table 1, entries 6,7 and 8), while DMF and DMSO yielded moderate amounts of products after 10 min (Table 1, entries 9 and 10). The effect of the catalyst to substrate molar ratio on the reaction was investigated in a model reaction to analyze and optimize the catalytic system. It was found that the use of a 5 % mole ratio of the catalyst to the substrate generated a low yield even after a relatively longer reaction time. In contrast, a 10% mole ratio of the catalyst to the substrate boosted the yield of the product by 85%. Further increasing the molar ratio of the catalyst to the substrate did not significantly change the yield of the product (Table 1, entries 1, 2, 3, and 4). The solvent of HOAc delivered suitable yields in the range of 75-98%. The highest yield (98%) was obtained when the reaction was performed at 120 °C for 5 min in the presence of acetic acid as the solvent and 10 mol% of ChCl: $ZnCl_2$ (1:2 mole/mole) as the catalyst (Table 1, Entry 5). Also, the yield increased from 85% to 90% with an increase in ChCl: $ZnCl_2$ (1:2 mole/mole) as the catalyst from 5 to 15 mol % (Table 1, entries 6 and 7)**.**

Regarding the mechanism, the reaction proceeds via the nucleophilic addition of the amine group of *o*-phenylene diamine to the carbonyl group of benzil. The electron-donating group on the aromatic ring of *o*-phenylene diamine facilitates nucleophilic attack to the carbonyl group of benzil. Also, electron-withdrawing groups on the phenyl ring of benzil increase the electrophilic tendency of its carbonyl group. Based on the mechanism and structure of the catalyst, ChCl:2$ZnCl_2$ as a green catalyst can play a triple role. (i) The ammonium ion of the choline group [$(CH_3)_3N^+(CH_2CH_2OH)$] induces the polarization of the carbonyl groups, (ii) The OH group of the choline activates carbonyl group by forming hydrogen bond, (iii) Zn^{2+} ions as Lewis acid promote the carbonyl group for the nucleophilic attack. The greater catalytic activity of ChCl: 2$ZnCl_2$ compared to ChCl: $ZnCl_2$ suggests that the role of Zn^{2+} ions is more critical than that of the ammonium ion and hydroxyl group in the catalyst.

The reactivity of diamine and diketones can be modified in all processes by changing the reaction times. For example, less sensitive systems containing substituted 1,2-phenylenediamines bearing electron-withdrawing groups (EWG) (Table 2, entries 5 and 8) and diketone (Table 2, entries 4 and 6) were more gently reduced and needed longer reaction times for computable alteration to desired products. We compared a number of the products synthesized using previously published methods with that generated by our proposed procedure (Table 2).

Table 2. Synthesis of quinoxaline derivatives according to the scheme 3.

Entry	Product (3)	G	R1	R2	Time (min.)	Yield (%)	m.p. (found)	m.p (reported)	Reference
1	3a	H	H	H	10	98	124-126	128-129	[35]
2	3b	NO_2	H	H	15	92	187-189	193-194	[35]
3	3c	CH_3	H	H	10	94	113-115	116-117	[36]
4	3d	H	NO_2	H	10	94	205-206	-----	
5	3e	NO_2	NO_2	H	15	96	250-251	-----	
6	3f	CH_3	NO_2	H	10	90	218-217	-----	
7	3g	H	H	Br	10	85	193-194	195-197	[37]
8	3h	NO_2	H	Br	15	90	183-186	-----	
9	3j	H	H	OMe	10	91	145-147	151-152	[35]
10	3k	NO_2	H	OMe	03:10	91	188-189	184-186	[35]
11	3l	CH_3	H	OMe	10	90	124-126	125-127	[38]

Many efforts have been devoted to enhancing the biological properties of quinoxaline, such as the introduction of functional groups to its aromatic rings [13]. It is known that the functional group incorporated in an aromatic ring can be converted to other functional group by transformation reactions. For example, the nitro groups can be converted to amine by reduction reactions, and the obtained diamines can be used for producing of polyamide, polyimide, polyurea, as well as for curing of epoxy resin [39-42]. Also, quinoxalines carrying two carbon-bromine bonds can be used to prepare polymers based on the coupling reactions of Suzuki, Heck, Sonogashira, and Buchwald [43-46].

In the same vein, the synthesis of quinoxaline derivatives bearing functional groups has been a topic of considerable interest. There are two general methods for the introduction of functional groups to the quinoxaline nucleus; a) via electrophilic substitution and b) using suitable synthon-bearing functional groups. The presence of electronegative nitrogen atoms in quinoxaline reduces its electron density, and therefore, quinoxaline ring has little activity against electrophilic substitution reagents. The electrophilic substitution reaction on quinoxaline ring occurs only under forcing condition, resulting in the formation of several low-yield products. For example, the nitration process was carried out only under harsh conditions (Conc. HNO_3, Oleum, 90 ˚C), resulting in the formation of two compounds: 5-nitroquinoxaline (1.5%) and 5,7-dinitro-quinoxaline (24%).

Conclusion

In the present study, a simple and efficient catalyst was developed using deep eutectic solvents to prepare novel quinoxaline derivatives in a one-pot reaction. The advantages of the prepared catalyst included easy preparation, low price, good stability, reusability, easy separation and purification from the reaction mixture, and being environmentally friendly. The catalyst also showed an outstanding yield for preparing quinoxaline derivatives under suitable conditions in terms of temperature and reaction time in a non-toxic solvent.

In addition, the presence of functional groups on quinoxaline rings can render them suitable moieties for certain applications, such as monomers to be used for preparing of polymers or as curing agents for fabricating thermoset polymers. A great attempt to synthesis of polymers from the quinoxaline derivatives is in progress and will soon be published elsewhere.

References

[1] F. Xu, G. Cheng, H. Hao, Y. Wang, W. Xu, D. Chen, D. Peng, Z. Liu, Z. Yuan, M. Dai, *Front. Microbiol.*, 7, 1948 (2016).

[2] M. El-Atawy, E. Hamed, M. Alhadi, A. Omar, *Molecules*, 24 (22), 4198 (2019).

[3] M. Montana, V. Montero, O. Khoumeri, P. Vanelle, *Molecules*, 25, 25122784 (2020).

[4] D.K. Pandey, T. Devadoss, N. Modak, R. Mahesh, *Indian J. Med. Res.*, 44, 614 (2016).

[5] G. Rajamanickam, J. Selvaraj, S. Selvaraj, T. Rajendran, M.M.R. Serkar, *J. Chem. Pharm. Sci.*, 8, 655 (2015).

[6] S.K. Lin, *Molecules*, 1, 37 (1996).

[7] X. Hui, J. Desrivot, C. Bories, P.M. Loiseau, X. Franck, R. Hocquemiller, B. Figadère, *Bioorg. Med. Chem. Lett.*, 16, 815 (2006).

[8] D.P. Singh, S.R. Hashim, R.G. Singh, *Int. J. Drug Dev. Res.*, 2, 810 (2010).

[9] T. Laabaissi, F. Benhiba, M. Missioui, Z. Rouifi, M. Rbaa, H. Oudda, A. Guenbour, *Heliyon*, 6, 03939 (2020).

[10] P.F. Frigerio, L.H. Tagle, F.R. Diaz, *Polymer*, 22, 1571 (1981).

[11] A.P. Kulkarni, Y. Zhu, S.A. Jenekhe, *Macromolecules*, 38, 1553 (2005).

[12] H. Khatoon, E. Abdulmalek, *Molecules*, 26, 1055 (2021).

[13] M. Soleymani, M. Chegeni, *Curr. Org. Chem.*, 23, 1789 (2019).

[14] K. Watanabe, H. Oguri, H. Oikawa, *Curr. Opin. Chem. Biol.*, 13, 189 (2009).

[15] M.R. Islami, Z. Hassani, *ARKIVOC*, XV, 280 (2008).

[16] D. Aparicio, O.A. Attanasi, P. Filippone, R. Ignacio, S. Lillini, F. Mantellini, F. Palacios, J.M.D.L. Santos, *J. Org. Chem.*, 71, 5897 (2006).

[17] H.M. Meshram, G.S. Kumar, P. Ramesh, B.C. Reddy, *Tetrahedron Lett.*, 51, 2580 (2010).

[18] S. Antoniotti, E. Duñach, *Tetrahedron Lett.*, 43, 3971 (2002).

[19] A. Mulik, D. Chandam, P. Patil, D. Patil, S. Jagdale, M. Deshmukh, *J. Mol. Liq.*,179, 104 (2013).

[20] D. Villemin, B. Martin, *Syn. Comm.*, 25, 2319 (1995).

[21] A.Kumara, T.M. Dhameliya, K. Sharma, K.A.Patel, R.V.Hirani, A.J. Bhatt, *J. Mol. Struct.*, 1259, 132732 (2022).

[22] A. Hasaninejad, A. Zare, M. Shekouhy, A.R. Moosavi-Zare, *E-J. Chem.*, 6, S247 (2009).

[23] B. Malek, I. Bahammou, O. Zimou, A. El Hallaoui, R. Ghailane, S. Boukhris, A. E. Souizi, *J. Turk. Chem. Soc. Sect. A Chem.*, 7, 427 (2020).

[24] Z. An, M. Wu, J. Ni, Z. Qi, G. Yu, R. Yan, L.B. Zhao, *Chem. Commun.*, 53, 11572 (2017).

[25] R. Sharma, C. Sharma, *Catal. Commun.*, 12, 327 (2011).

[26] A. Shaabani, A.H. Rezayan, M. Behnam, M. Heidary, *Comptes Rendus Chim.*, 12, 1249 (2009).

[27] J.J. Cai, J. Zou, X.-Q. Pan, W.G. Zhang, *Tetrahedron Lett.*, 49, 7386 (2008).

[28] M.D. Argyle, C.H. Bartholomew, *Catalysts*, 5, 145 (2015).

[29] K.N. Marsh, A. Deer, A.C-T. Wu, E. Tran, A. Klamt, *Korean Chem. Eng.*, 19, 357 (2002).

[30] D.A. Alonso, A. Baeza, R. Chinchilla, G. Guillena, I.M. Pastor, D.J. Ramón, *Eur. J. Org. Chem.*, 2016, 612 (2016).

[31] E.L. Smith, A.P. Abbott, K.S. Ryder, *Chem. Rev.*, 114, 11060 (2014).

[32] G. Nithya, C.C. Kanakam, R. Sudha, V. Vanitha, *Int. J. Chem. Biomed. Sci.*, 1, 25 (2015).

[33] H. Kinger, W. Martinoff, *Annalen*, 389, 232 (1912).

[34] Y. Zou, H. Xu, G. Wu., Z. Jiang, S. Chen, Y. Huang, W. Huang, X. Wei, *J. Phys. Chem. B*, 113, 2066 (2009).

[35] S. Sajjadifar, S. Miri, *Int. J. Chemtech. Res.*, 6, 5433 (2014).

[36] S. Sajjadifar, M.A. Zolfigol, S.A. Mirshokraie, S. Miri, O. Louie, E. Rezaee Nezhad, S. Karimian, G. Darvishi, E. Donyadari, S. Farahmand, *Am. J. Org. Chem.*, 2, 97 (2012).

[37] B.B. Popatkar, G.A. Meshram, *Heterocycles*, 100, 1009 (2020).

[38] G. Mohammadi Ziarani, A. Badiei, M. Haddadpour, *Int. J. Chem.*, 3, 87 (2011).

[39] A. Sadeghinia, H. Mighani, *Chem. Method.*, 4, 115 (2020).

[40] H. Mighani, M. Ghaemy, *Chinese J. Polym. Sci.*, 28, 147 (2010).

[41] M. Ghaemy, H. Behmadi, *J. Appl. Polym. Sci.*, 107, 4021 (2008).

[42] M. Ghaemy, R. Alizadeh, H. Behmadi, *Eur. Polym. J.*, 45, 3108 (2009).

[43] W. Liu, X. Luo, Y. Bao, Y.P. Liu, G.H. Ning, I. Abdelwahab, L. Li, C.T. Nai, Z.G. Hu, D. Zhao, B. Liu, S.Y. Quek, K.P. Loh, *Nat. Chem.*, 9, 563 (2017).

[44] M.A. Andrade, L.M.D.R.S. Martins, *Molecules*, 25, 5506 (2009).

[45] C.G. Frost, P. Mendonça, *J. Chem. Soc., Perkin Trans. 1*, 16, 2615 (1998).

[46] R. Dorel, C.P. Gurgel, A.M. Haydl, *Angew. Chem. Int. Ed.*, 58, 17118 (2019).