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Sodium toluene-4-sulfonate Catalyzed Microwave Assisted Efficient Synthesis and Antimicrobial Assay of Substituted 2-aryl benzoxazoles in Aqueous Medium

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ABSTRACT

The 2- substituted benzoxazoles have been found to be excellent key motif which shows broad spectrum of biological activity because of this it has great interest for the development of newer methods of synthesis. We predicted that the use of sodium toluene-4-sulfonate as catalyst in aqueous medium for synthesis of 2-substituted benzoxazoles provides an alternative green pathway for these bioactive compounds. In the present work we report environmentally benign synthesis of benzoxazoles from 2-amino phenol and substituted aromatic carboxylic acids by using sodium toluene-4-sulfonate catalysis under microwave irradiation in aqueous medium and antimicrobial evaluation of synthesized benzoxazoles.

Keywords: sodium toluene-4-sulfonate, 2-aryl benzoxazoles, microwave, aqueous medium, antimicrobial assay.

INTRODUCTION

A large number of heterocyclic compounds are important for the life because of their unique biological activity. They occupied enormous significances due to their interesting and diverse pharmaceutical applications in the field of medicinal chemistry[1]. Benzoxazoles are class of important scaffolds and acts as intermediate in synthesis of various bioactive molecules like precursors for biosensors coupling, in synthesis of amino acid and peptides as

well as photosensitive composition device for proteins and wide range of pharmaceutical activities[2]. They are of immense importance heterocyclic compounds because they exhibit wide variety of biological activities such as antibacterial and antifungal, antiperkinson, anti-tuberculosis, anticancer, anti-inflammatory and analgesic, antitumor, antibiotic, thus leading them to becoming interesting molecular structure in drug designing. In addition to this benzoxazoles are of great importance in material science, especially in fluorescent material[3-12]. In the point of view, the new series of 2-arylbenzoxazoles based on docking study, it has been identified as potential $A_{2A}R$ antagonists. The micromolar affinity to words $A_{2A}R$ antagonists because of structure –affinity relationship was investigated in position 2, 5 and 6 of the benzoxazole.[13]. They are most frequently encountered as building block of many drugs, pharmaceutically relevant substances and agrochemicals[14-15]. Some examples including benzoxazole subunit which were found in commercial drugs like cathepsins inhibitor, ERB-041 (estrogen receptor-β agonist), JTP- 426467 (selective peroxisome proliferator activated receptor γ antagonist), Flunoxaprofen (NSAID), NSC-693638 (anticancer agent)[16-18]. The number of important natural product have benzoxazole ring system such as UK-1, AJI9561, Pseudopteroxazole and Salvianen[19-21] (Fig. 1).

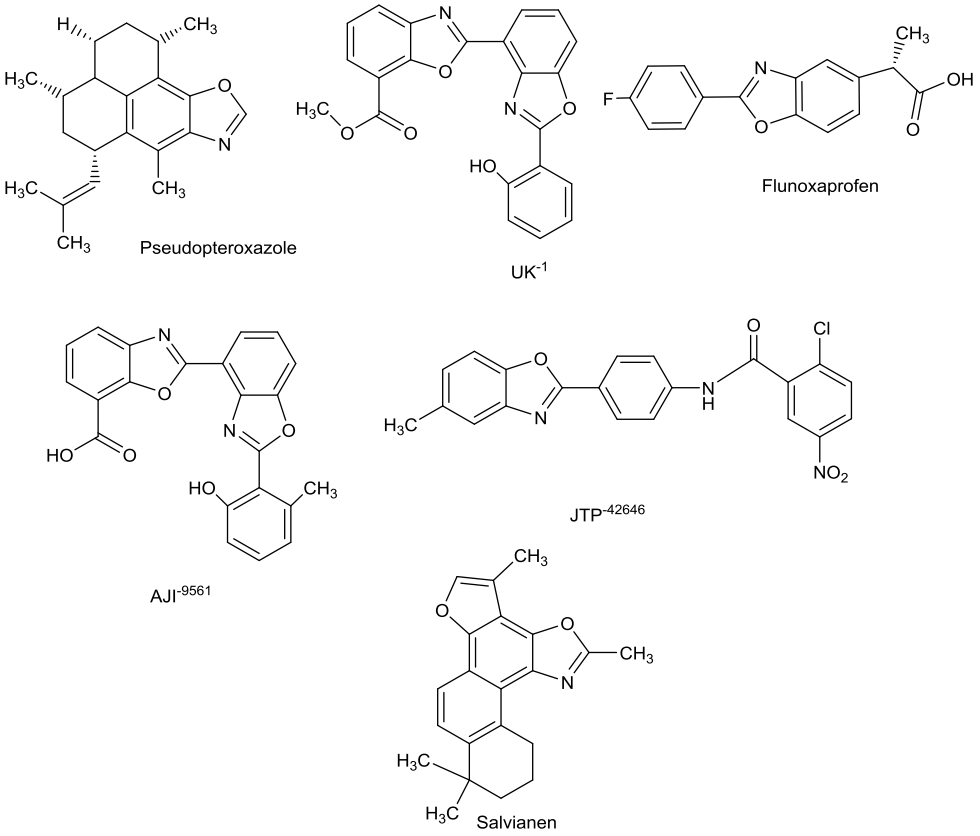
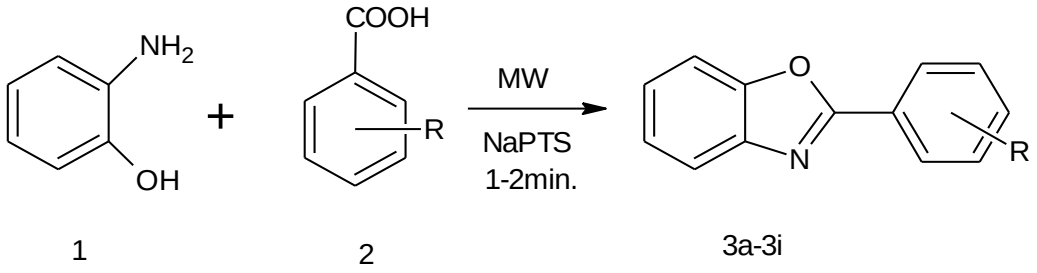


Fig.1: Naturally occurring and biological important compounds with benzoxazole moiety

In addition to these, some biologically active compounds containing benzoxazole moiety, which acts as agrochemicals such as herbicide Fenoxaprop[22-24]. In the last few decades, the transition–metal catalyzed synthesis for making carbon-heteroatom bond have been developed for the formation of biological active hetrocycles. It includes transition metal like copper; palladium; cobalt and iron-catalyzed[25-28] intramolecular cyclization of 2-haloanilides have been used for the synthesis of benzoxazoles moiety[29-30]. For the synthesis of 2-benzoxazole derivatives there are two methods, one is involving coupling of 2-aminophenols with derivatives of carboxylic acid catalyzed by strong acid or by microwave heating as a green protocol[31-32]. In another method, the oxidative cyclization of phenolic Schiff bases formed by the condensation of 2-aminophelos and aldehydes. For this transformation various oxidants like DDQ, Mn-(OAc), $PhI(OAc)_2$,$Th^{+\cdot}ClO_4^-$, $BaMnO_4$, NiO_2 and Pb-$(OAc)_4$ have been used[33-39]. In the paper we report, the use of sodium toluene-4-sulfonate as catalyst in aqueous medium for synthesis of 2- substituted benzoxazoles provides an alternative green pathway for these bioactive compounds.

RESULTS AND DISCUSSION

Green and sustainable environment have considerable attention all over the globe because of the pollution. It is necessary to use environmental benign protocol or methodology for organic transformation which reduce the pollution some extent. In present work, we report here the environmental sustainable organic transformation in aqueous medium under microwave irradiation. Here both the protocol such as water for aqueous medium acts as universal solvent and microwave irradiation acts as conventional energy source which save the energy. For the synthesis of benzoxazoles we report herein the aqueous medium of Sodium toluene-4-sulfonate. The sodium toluene-4-sulfonate in aqueous medium acts acidic medium which proceed with the organic transformation of benzoxazoles derivatives. The sodium toluene-4-sulfonate generally acts as a hydrotrope. Basically hydrotropes are increase solubility of sparingly soluble organic compounds aqueous medium[40]. It is a water- soluble and surface active compounds; they significantly increase the solubility of organic solutes such as esters, alcohols, ketones, aldehydes, hydrocarbons and fats [41-42]. Most hydrotropic solutions precipitate the solute on dilution with distilled water therefore recovery and re-use of hydrotropic solvent is easy[43]. It has number of applications and used for many purposes such as drug solubilization, detergent formulations, health care, in household applications[44], also used as extracting agent. Overall hydrotrope has various application as well as it used as green catalyst for organic transformation. The microwave is the conventional energy source it save the energy and acts as a sustainable development in organic transformation. Therefore here use one of the hydrotrope is sodium paratoulene sulfonate (NaPTS) for synthesis of benzoxazoles derivatives. In the present work we report environmentally benign synthesis of benzoxazoles from 2-amino phenol and substituted aromatic carboxylic acids by using sodium toluene-4-sulfonate catalysis under microwave in aqueous medium and antimicrobial evaluation of synthesized benzoxazoles (Scheme-1).



Scheme 1: Synthesis of Benzoxazoles under microwave in aqueous medium

The screening of aqueous medium with different hydrotropes such as sodium toluene-4-sulfonate (NaPTS), sodium benzene sulfonate (NaBS) and sodium xylene-4-sulfonate (NaXS) are at room temperature and under microwave irradiation were selected for this purpose as shown in Table No. 1.1 We opted to use 50 % (w/v) aqueous solutions of selected hydrotropes in aqueous medium, since this concentration was suitable for the maximum solubilization of organic compounds Friberg *et al*. (1996). When reaction completed, with water the reaction mixture was diluted and the filtration of reaction mixture followed by recrystallization of solid the corresponding product of a high purity were obtained. The comparison of the model reaction was performed at room temperature it requires longer reaction time was required as compared to microwave. As excellent results were obtained for NaPTS, we employed this particular hydrotrope for subsequent studies for the synthesis of 2-aryl benzoxazole derivatives.

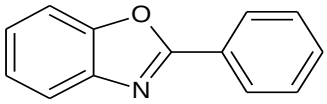
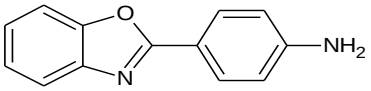
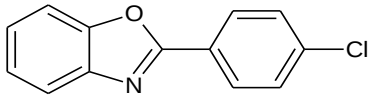
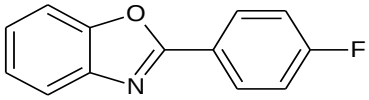
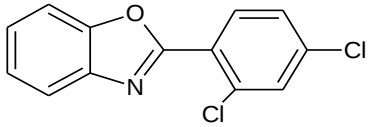
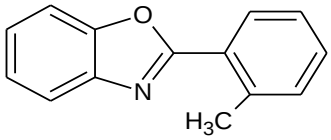
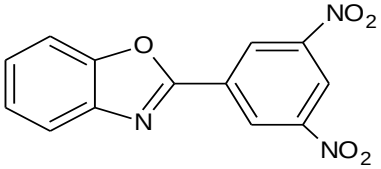
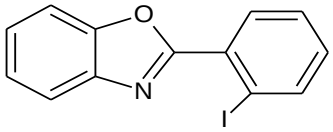
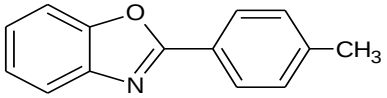
Table No.1.1: Screening of aqueous hydrotropic medium for synthesis of 2-aryl benzoxazoles[a]

Entry	Hydrotropes	With Microwave [b]		Room Temp. [c]	
		Time (min.)	Yield [d] (%)	Time (h)	Yield [d] (%)
1	sodium toluene-4-sulfonate (NaPTS)	2	92	1	75
2	sodium xylene-4-sulfonate (NaXS)	15	75	2	55
3	sodium benzene sulfonate (NaBS)	28	60	3.5	40

a Reaction conditions: 2-aminophenol (1.0 mmol), carboxylic acid (1.0 mmol), aqueous hydrotropic solution (5 mL).
b Reactions under microwave irradiation.
c Reactions at room temperature.
d Isolated yields after purification.

In the present work considering greener and sustainable approach, we have used sodium toluene-4-sulfonate as catalyst in aqueous medium for synthesis of substituted benzoxazoles by cyclization of 2-amino phenol and carboxylic acids under microwave irradiation. We carried out the cyclisation reaction between 2-amino phenol and different substituted benzoic acid in presence of sodium toluene-4-sulfonate as a catalyst under microwave irradiation for 1-2 minute targeted substituted 2-arylbenzoxazoles (3a-3i) and product obtained in good yield as shown in Table No. 1.2.

Table 1.2: synthesis of 2-(4-substituted aryl) benzoxazoles[a]

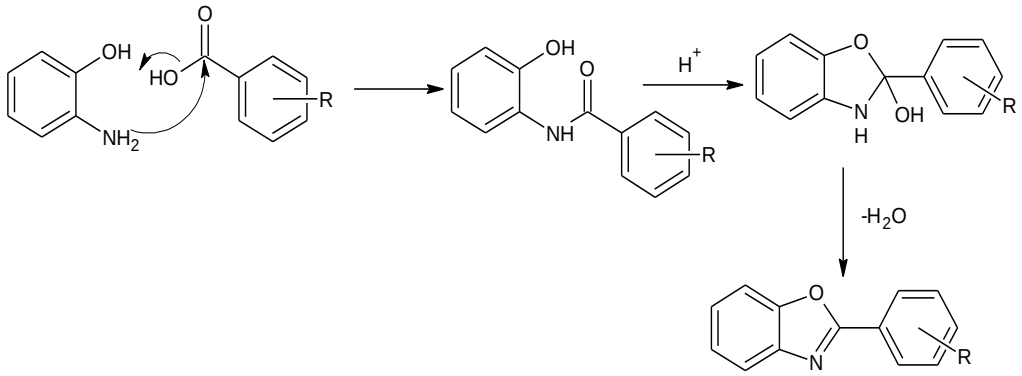
Sr No.	Entry	Compound [a]	Yield[b] (%)	MP[c] (^{0}C)
1	3a		92	100 [100- 102]
2	3b		90	115 [115-120]
3	3c		88	144 [144-145]
4	3d		86	94-96
5	3e		85	118-119 [118-119]
6	3f		82	68 [68-69]
7	3g		80	206 [205-207]
8	3h		78	150-153
9	3i		86	115[114-116]

All products were characterized by IR, ^{1}HNMR, ^{13}CNMR, Mass spectroscopy.

[b] Isolated yields after purification.

[c] Literature value in parenthesis.

The proposed reaction mechanism for synthesis of 2-substituted benzoxazoles from 2-amino phenol and various substituted aromatic acids is outlined in **Scheme 1.2.**



Scheme 1.2: A Plausible reaction mechanism for synthesis of benzoxazole derivatives in aqueous medium under microwave.

The structures of the products were determined by IR, ^{1}H NMR and^{13}C NMR spectroscopy as well as by mass spectrometry and their values obtained are in good harmony with literature values. The synthesized 2-substituted benzoxazoles (3a-3i) was identifying on the basis of IR, ^{1}H NMR and^{13}C NMR spectroscopy and physical constant. The physical and spectroscopic data were in full agreement with the proposed structure.

All the synthesized derivatives of benzoxazoles were assayed for their in vitro antibacterial activity against S.aureus (gram positive), E.coli (gram negative) and antifungal activity was screened against A. Niger by using cup-plate method. All the antimicrobial results of tested compounds 3a-3i are given in table 1.3. The compounds 3b, 3c, 3f shows good antibacterial activity against S.aureus. The derivatives of benzoxazole from 3a-3i show excellent antibacterial activity against E.coli. The other derivative from 3b to 3i gives high potent antifungal activity against A. Niger. This compare with standard fluconazole. Remaining compounds shows moderate activity.

Table 1.3 - Antimicrobial analysis of synthesized compounds (3a-3i):

Compound No.	Antibacterial activity		Antifungal activity
	S.aureus	E.coli	A.niger
3a	17	11	12
3b	**26**	15	**18**
3c	**21**	16	**19**
3d	17	17	**22**
3e	16	23	**22**
3f	**25**	17	13
3g	17	18	**22**
3h	18	19	12
3i	17	18	**16**
Std flucanazole	-	-	17
Std streptomycin	28	11	-

EXPERIMENTAL

All chemicals were purchased from Loba and Sigma Aldrich chemical companies and usedfor the synthesis without further purification. Melting points were determined in an melting point apparatus and are uncorrected. The purity of compound checked by the TLC. The microwave synthesizer used for the synthesis of compounds. The Fourier transform infrared spectroscopy was performed by FTIR, Lambda, Australia, in the form of diluted sample (10 wt.%) pressed into KBr pellets. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avon 300 MHz spectrometer using $CDCl_3$ as solvent and TMS as internal standard

Synthesis of 2-(substituted aryl) benzoxazoles:

A mixture of 2-amino phenol (0.01mol), substituted carboxylic acids (0.01mol) and 10 ml aqueous solution of sodium toluene-4-sulfonate was taken in beaker and irradiated in micro-oven for one to two minute. The completion of reaction monitored by TLC. The reaction mixture was poured on ice cold water and crude product obtained was filtered and recrystallized from ethanol.

Recyclability Study

The reuse of catalyst is the significant approach for organic transformation because it directly effects on cost of methodology and sustainability of the environment. The catalyst recovery is achieved after filtration of product, collect the filtrate and by simple evaporation the catalyst is concentrated and which is ready to use for another organic transformation. We check the recyclability of sodium toluene-4-sulfonate by 5 times and it shows good result with loss of small amount of yield which is shown in fig. 2.

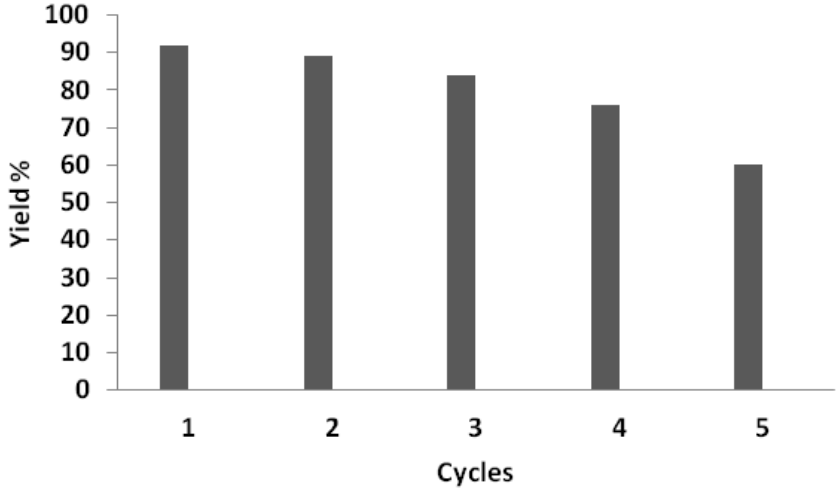


Fig. 2: Recyclability of sodium toluene-4-sulfonate

Spectral analysis:

2-Phenylbenzoxazole (Table 1.2, entry 3a):

IR (KBr, thin film): υ = 3056, 2950, 2918, 2840, 1614, 1555, 1472, 1445, 1340 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.31-8.28 (2H, m, Ar-H), 7.81-7.80 (1H, m, Ar-H), 7.63-7.50 (4H, m, Ar-H), 7.39-7.35 (2H, m, Ar-H).ppm ^{13}C NMR (75 MHz, CDCl3): δ 163.0, 151.2, 141.8, 131.4, 128.4, 127.7, 127.2, 125.2, 124.7, 119.6, 110.4 MS (EI): m/z =195 (M+).

4-(1,3-benzoxazol-2-yl)aniline(Table 1.2, entry 3b):

IR (KBr, thin film): υ =3376, 3052, 2953, 2918, 2844, 1616, 1555, 1472, 1446, 1343 cm^{-1}. ^1H NMR (300 MHz, CDCl3): δ 8.18-8.15 (2H, dd, *J* = 7.5, 1.7 Hz, Ar-H), 7.77-7.74 (1H, m, Ar-H), 7.58-7.56 (1H, m, Ar-H), 7.48-7.44 (2H, m, Ar- H), 7.37-7.28 (2H, m, Ar-H). ^{13}C NMR (75 MHz, CDCl3): δ 162.7, 150.0, 141.5, 145.6, 128.3, 128.0, 124.8, 123.8, 119.1, 110.6. MS (EI): m/z =210 (M+).

2-(4-Chlorophenyl)benzoxazole (Table 1.2, entry 3c):

IR (KBr, thin film): υ = 3083, 3057, 1617, 1596, 1553, 1483, 1452, 1404, 1349 cm^{-1}. ^1H NMR (300 MHz, CDCl3): δ 8.16-8.13 (2H, dd, *J* = 7.5, 1.7 Hz, Ar-H), 7.75-7.72 (1H, m, Ar-H), 7.56-7.54 (1H, m, Ar-H), 7.48-7.45 (2H, m, Ar- H), 7.38-7.29 (2H, m, Ar-H).ppm ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.2, 150.7, 141.9, 137.7, 129.2, 128.8, 125.6, 125.3, 124.7, 120.0, 110.6. MS (EI): m/z = 231(M+).

2-(4-Fluorophenyl)benzoxazole **(Table 1.2, entry 3d):**

IR (KBr, thin film): υ = 3064, 3055, 1617, 1595, 1552, 1486, 1452, 1405, 1349, 1294,1247, 1198, 1175, 1107, 1092,1056, 1012 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$,): δ 8.25 (d, 2H, Ar–H), 7.79 (t, 1H, Ar–H), 7.56 (t, 1H, Ar–H), 7.38 (d, 2H, Ar–H), 7.22 (d, 2H, Ar–H)ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.6, 162.2, 150.8, 141.8, 129.7, 129.7, 125.0, 124.5, 123.3, 119.8, 116.2, 115.8, 110.4; MS (70 eV, EI): *m/z* (%): 214 (M+1).

2-O-Tolylbenzoxazole (Table 1.1, entry 3f):

IR (KBr, thin film): υ = 3054, 3022, 2915, 2850, 1622, 1552, 1501, 1472, 1449,1409, 1345,1312, 1285, 1242,1197,1176,1139, 1115,1053, 1016 cm^{-1} ^1H NMR (300 MHz, $CDCl_3$): δ 8.18-8.16(m,1H, Ar-H), 7.83-7.79 (m,1H Ar-H), 7.60-7.57 (m,1H Ar-H),7.42-7.23 (m,5H, Ar-H), 2.81 (s,3H CH3); ^{13}C NMR (75 MHz, $CDCl_3$): 163.4, 150.3, 142.1, 138.8, 131.7, 130.1, 129.9, 126.2, 126.0,125.0, 124.3, 120.1, 110.4, 22.2 (CH_3) MS (EI): m/z = 209 (M+).

2-p-Tolylbenzoxazole (Table 1.1, entry 3i):

IR (KBr , thin film): υ = 3054,3022,2915,2848,1622,1551, 1549, 1472, 1449, 1408, 1344cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.18-8.16 (2H, m, Ar-H), 7.77 (1H, m, Ar-H), 7.61-7.58 (1H, m, Ar-H),7.34-7.27 (4H, m, Ar-H), 2.45 (3H, s, CH3).ppm ^{13}C NMR (75 MHz, $CDCl_3$): 164.3, 151.4, 142.2, 142.1, 129.6,127.5, 124.8, 124.4, 124.2, 119.6, 110.4, 21.4 (CH_3). MS (EI): m/z = 210 (M+1).

CONCLUSION

We have used ecofriendly microwave assisted synthetic method for synthesis of substituted benzoxazole derivatives in aqueous medium. It is found that sodium toluene-4-sulfonate is an efficient catalyst in aqueous medium for the synthesis of 2-aryl benzoxazoles. Experimental simplicity, simple and readily available starting material, broad scope of synthesized compounds, green cyclizing agent, non-toxic nature of catalyst, short reaction time, high yield, has capacity for large scale synthesis are the features of current synthesis. Some of these synthesized benzoxazole derivatives shows good antifungal and antibacterial activity.

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REFERENCES

1. Kunied, T.; Mutsanga, H. *The chemistry of heterocyclic compounds, Palmer, B,* 175, (2002).
2. Demmer CS, Bunch L. Benzoxazoles and oxazolopyridines in medicinal chemistry studies. *Eur J Med Chem.* 97:778–785, (2015).
3. Kaspady, M.; Narayanswamy, V.K.; Raju, M.; Rao, G.K. *Lett. Drug Des. Disc.*, 6, 21-28, (2009).
4. Benazzou, A.; Boraund, T.; Dubedat, P.; Boireau, J.M.; Stutzmann, C. *Eur.J. Pharmcol.*, 284, 299-307, (1995).
5. Moraski, G.C.; Chang, M. *Eur. J. Med. Chem.*, 45, 5, 1703-1716, (2010).
6. Fatih, M. U.;Craig , J .F. Bioorganic and *Med. chem. lett.*, 11,9,1181-1183, (2001).
7. Goksen, U.S.; Kelekci, N.G.; Goktas, O.; Koysal, Y.; Kilic, E.; Isik, S.; Aktay, G.; Ozalp, M. *Bioorganic &Medicinal Chemistry*,15,5738–5751, (2007).
8. Sierra, F.M.P.; Pierre, A.; Burbridge, M.; Guilbaud, N. *Bioorganic and Medicinal Chemistry Letters.*, 12, 1463–1466, (2002).
9. Ranabir, S.R.; Neil, L.K.; Jill, C.M.; Christopher, T.W. *Chemistry and Biology*, 6, 5, 305-318, (1999).
10. Evindar, G.; Batey, R.A. *J. Org. Chem.*,71, 1802-1808, (2006).
11. Boyer, J.; Arnoult, E.; Médebielle, M.; Guillemont, J.; Unge, J.; Jochmans, D.; *J. Med. Chem.*, 54, 797, (2011).

12. R. Duroux, N. Renault, J. E. Cuelho, L. Agouridas, D. Blum, L. V. Lopes, P. Melnyk, and S. Yous, J *Enzyme Inhib Med Chem*., 32(1): 850, (2017).
13. (a) Oksuzoglu,E.; Tekiner-Gulbas,B.; Alper, S.; Temiz-Arpaci,O.; Ertan,T.; Yildiz, I.; Diril, N.; Sener-Aki, E.; Yalcin, I.J. *J. Enzyme Inhib. Med.Chem.,* , 23, 37, (2008); (b) Oksuzoglu, E.; Temiz-Arpaci,O.; Tekiner-Gulbas, B.; Eroglu,H.; Sen, G.; Alper,S.; Yildiz, I.; Diril, N.; Aki-Sener, E.; Yalcin, I. *Med. Chem. Res.*, 16, 1, (2007).
14. McKee,M.L.; Kerwin, S.M. Bioorg. Med. Chem., 16, 1775 (2008).
15. Tully, D. C.; Liu, H.; Alper, P. B.; Chatterjee, A. K.; Epple, R.; Roberts, M. J.Williams, J. A.; Nguyen, K. T.; Woodmansee, D. H.; Tumanut, C.; Li, J.; Spraggon, G.; Chang, J.; Tuntland, T.; Harris, J. L.; Karanewsky, D. S. *Bioorg. Med. Chem. Lett.*,16, 1975, (2006).
16. Leventhal, L.; Brandt, M.R.; Cummons, T.A.; Piesla, M.J.; Rogers, K.E.; Harris H.A.; *Eur. J. Pharmacol.* 553, 146, (2006).
17. Nishiu, J.; Ito, M.; Ishida, Y.; Kakutani, M.; Shibata, T.; Matsushita, M.; Shindo, M. *Diabetes Obes. Metab.*, 8, 508 (2006).
18. Kallashi, F.; Kim. D.; Kowalchick, J.; Park ,Y. J.; Hunt, J.A.; Ali, A.; SmithC.J.; Hammond, M.L.; Pivnichny, J.V.; Tong, X.; Xu, S.S.; Anderson , M.S.;Chen Y.; Eveland ,S.S.; Guo, Q.; Hyland, S.A.; Milot, D.P.; Cumiskey, A.M.; Latham, M.; Peterson, L.B.; Rosa, R., Sparrow, C.P.; Wright, S.D.; Sinclair, P.J.; *Bioorg. Med. Chem. Lett.*, 21, 558, (2011).
19. Easmon, J.; Pürstinger, G.; Thies, K.S.;Heinisch , G.; Hofmann ,J.; J. *Med.Chem.*, 49, 6343, (2006).
20. Ueki, M.; Ueno, K.; Miyadoh, S.; Abe, K.; Shibata, K.; Taniguchi, M.; Oi, S. *J.Antibiot.*,46, 1089,(1993).
21. Sato, S.; Kajiura, T.; Noguchi, M.; Takehana, K.; Kobayashi, T.; Tsuji, T. J. *Antibiot.* 2001, 54, 102, (2001).
22. Viirre , R.D.; Evindar ,G.; Batey, R.A.; *J. Org. Chem.*, 73, 3452, (2008).
23. a) A. Ahmed, R. Singha, J. K. Ray, *Tetrahedron Lett.*, , 56, 2167, (2015); b) Y. Wang, C. Wu, S. Nie, D. Xu, M. Yu, X. Yao, *Tetrahedron Lett.*,56, 6827,(2015); c) N. Khatum, S. Guin, S. K. Rout, B. K. Patel, *RSC Adv.*, 4,10770, (2014) d) M. Mohammadi, G. R. Bardajee, N. N. Pesyan, *RSC Adv.*, 4, 62888, (2014); e) F. Wu, J. Zhang, Q. wei, P. Liu, J. Xie, H. Jiang, B. Dai, *Org. Biomol. Chem.*, 12 9696, (2014); f) R. D. Viirre, G. Evindar, R. A. Batey; *J. Org. Chem.*,73, 3452,(2008); g) N. Barbero, M. Carril, R. SanMartin, E. Domínguez, *Tetrahedron*,63, 10425, (2007); f) G. Evindar, R. A. Batey; *J. Org. Chem.*, 71, 1802, (2006); g) G. Altenhoff, F. Glorius, *Adv. Synth. Catal.*, 346, 1661, (2004).
24. a) Y. Cheng, Q. Peng, W. Fan, P. Li, *J. Org. Chem.*, 79, 5812, (2014); b) C. Benedí, F. Bravo, P. Uriz, E. Fernández, C. Claver, S. Castillon, *Tetrahedron Lett.*,44, 6073, (2014).
25. a) J. He, F. Lin, X. Yang, D. Wang, X. Tan, S. Zhang, *Org. Process. Res. Dev.*, 20, 1093, (2016); b) R. Hajipour, Z. Khorsandi, M. Mortazavi, H. Farrokhpour, *RSC Adv.*,5,

107822,(2015) ; c) P. Saha, M. A. Ali, P. Ghosh, T. Punniyamurthy, *Org. Biomol. Chem.*, 8, 5692, (2010).
26. a) K. Gopalaiah, S. N. Chandrudu, RSC Adv., 2015, 5, 5015; b) J. Bonnamour, C. Bolm, Org. Lett., 10, 2665,.(2008).
27. a) K. T. Neumann, A. T. Lindhardt, B. Bang-Andersen, T. Skrydstrup, *Org. Lett.*,17, 2094, (2015); b) D. B. Nale, B. M. Bhanage, *Synlett*, 26, 2835,(2015) c) X. Zhang, W. Zeng, Y. Yang, H. Huang, Y. Liang, *Org. Lett.*,16, 876, (2014).
28. F. Abdellaoui, C. Youssef, H. B. Ammar, T. Roisnel, J.-F Soulé, H. Doucet, *ACS Catal.*, 6, 4248, (2016); b) A. R. Tiwari, B. M. Bhanage, *Org. Biomol. Chem.*,14, 7920, (2016); c) F. Zhu, J.-L Tao, Z.-X Wang, *Org. Lett.*,17, 4926, (2015); d) X.-B Shen, Y. Zhang, W.-X Chen, Z.-K Xiao, T.-T Hu, L.-X Shao, *Org. Lett.*, 16, 1984, (2014); e) D. M. Ferguson, S. R. Rudolph, D. Kalyani, *ACS Catal.*, 4, 2395, (2014); f) F. Gao, B.-S Kim, P. J. Walsh, *Chem. Commun.*,50, 10661, (2014); g) X. Zhang, W. Zeng, Y. Yang, H. Huang, Y. Liang, *Org. Lett.*, 2014, 16, 876, (2014); h) Q. Song, Q. Feng, M. Zhou, Org. Lett.,15, 5990, (2013). i) D. Liu, B. Liu, J. Cheng, *RSC Adv.*,3, 9193, (2013). j) Y. Cheng, Jun Yang, Yue Qu, P. Li, *Org. Lett.*,14, 98, (2012); k) K. Muto, J. Yamaguchi, K. Itami, *J. Am. Chem. Soc.*,134, 169, (2012); l) N. Park, Y. Heo, M. R. Kumar, Y.Kim, K. H. Song, S. Lee, *Eur. J. Org. Chem.*, 1984 (2012); m) K. Xie, Z. Yang, X. Zhou, X. Li, S. Wang, Z.Tan, X. An, C.-C Guo, *Org. Lett.*,12, 1564, (2010).
29. Terashima, M.; Ishii, M.; Kanaoka, Y. *Synthesis*, 484-485, (1982).
30. (a) Bourgrin, K.; Loupy, A.; Soufiaoui, M. *Tetrahedron*, 54, 8055-8064, (1998); (b) Pottorf, R. S.; Chadha, N. K.; Katkevics, M.; Ozola, V.; Suna, E.; Ghane, H.; Regberg, T.; Player, M. R. *Tetrahedron Lett.*, 44, 175-178, (2003).
31. Chang, J.; Zhao, K.; Pan, S. *Tetrahedron Lett.*, 43, 951-954(2002).
32. Varma, R. S.; Kumar, D. *J. Heterocycl. Chem.*, 35, 1539- 1540, (1998).
33. Varma, R. S.; Saini, R. K.; Prakash, O. *Tetrahedron Lett.*, 38, 2621-2622, (1997).
34. Park, K. H.; Jun, K.; Shin, S. R.; Oh, S. W. *Tetrahedron Lett.*,37, 8869-8870, (1996).
35. Srivastava, R. G.; Venkataramani, P. S. *Synth. Commun.*, 18, 1537-1544, (1988).
36. Nakagawa, K.; Onoue, H.; Sugita, *J. Chem. Pharm. Bull.*, 12, 1135-1138, (1964).
37. Stephens, F. F.; Bower, J. D. *J. Chem. Soc.*, 2971-2972, (1949).
38. S. B. Kamble, A. S. Kumbhar, S. N. Jadhav and R. S. Salunkhe. *Procedia Material Science*, 6, 1850-1856, (2014).
39. V. G. Gaikar, P.V. Phathak. *Sep. Sci. Technol.*, 34, 439-459, (1999).
40. S. E. Friberg, Hydrotropes. *Surf. Sci.*, 2, 490-494, (1997).
41. X. Chen, J. C.Micheu. *J. Colloid Interface Sci.*, 249, 172-179, (2002).
42. Mckee, H. Ralph. *Journal of Industrial and Engineering Chemistry*, 38, 382-384, (1946).
43. S. E. Friberg, C. Brancewicz. *Langmuir*, 10, 2945-29497, (1994)
44. W. Xiong , J. X. Chen, M.C. Liu, J. C. Ding, H. Y. Wu, W. K. Su . *J Braz. Chem. Soc*, 20, 367-374. (2009).