ScienSage

Journal of Advanced Scientific Research

Available online through http://www.sciensage.info/jasr

ISSN
0976-9595
Research Article

IONIC LIQUID ASSISTED GREEN SYNTHESIS OF 2-PHENYLIMIDIZO [4,5-*F*][1,10]- PHENANATHROLINE AT ROOM TEMPERATURE

Arshia Parveen

Department of Chemistry B. Raghunath College, Parbhani.431401

**Corresponding author: arshiachemistry@yahoo.co.in*

ABSTRACT

A range of 2-phenylimidazo [4,5-*f*] [1,10]-phenanthroline have been synthesized in very good yield under solvent-free conditions by grinding 1,10,phenanthroline-5dione,aromatic aldehydes and ammonium acetate in the presence of $[HBim]BF_4$ as catalyst. The short reaction time, clean reaction, and easy workup make this protocol practically economical attractive and efficient.

Keywords: 2-phenylimidazo [4,5-*f*] [1,10]- phenanthroline, aldehydes, 1,10,phenanthroline- 5dione , ammonium acetate.

1. INTRODUCTION

The Ru (II) metal complexes of 2-phenylimidazo [4,5-*f*] [1,10]-phenanthroline has been attracted considerable attention of chemist for many years [1],because their utilities in DNA structure prob [2, 3]. The heterocyclic compounds with fused imidazopyridine ring system represent an important class of ligand not only for their theoretical interest but also from a pharmacological point of view. These heterocyclic structures forms the skeleton of natural alkaloids [4] which act as neuromuscular blocking agent [5], reversible inhibitors of the H^+, K^+, ATPase enzyme [6] with a potent anti-secretory activity [7] and sedative hypnotics of the nervous system [8]. The imidazole-[1,5-a]pyridine is a basic structure of synthetic drugs such as Pirmogrel, with human clinical application as effective platelets aggregation and thromboxane synthase inhibitors [9] moreover, N, N-Bidentate ligands with mixed five and six membered heterocycles are a desirable class of compounds in pursuit of structural diversity to enhance the physical and chemical properties in particular, 1-pyridylimidazo-[1,5-a]-pyridines possessing a bidentate structural feature with a pyridyl nucleus adjacent to a fused imidazole have emerged as a new class of ligand which is a potential positive inotropic agents [10, 11].

Literature survey shows that synthesis of 2-phenylimidazo [4,5-*f*] [1,10]- phenanthroline has various routs like from 1,10,phenanthroline--5.6-dione with aldehyde in the presence of ammonium acetate in acetic acid [12] and anhydrous $ZnCl_2$ mediated the formation of 2-4,5-diphenyl-2-pyridin-2-yl-1H-imidazol-1-yl in methanol [13] and molecular iodine [14].

Most routes involve reaction of a 2-amino methyl pyridine with acylation followed by cyclization with phosphorus oxy chloride or polyphosphoric acid [15] or thiocyclation followed by ring closure using DCC or mercuric salts [16] Imidazo-[1,5-a]-pyridines were also obtained from 2-cynopyridine by the Vilsmeir reaction [17] or by reaction with Schiff bases in the presence of three steps from the dipyridyl ketone [18-22]. In 1882, Radziszewski report the first time synthesis of 2,4,5-triphenyl imidazoles [23, 24] and using nitriles and esters [25] also reported by using potassium ferrocynide [26]. Siddiqui et al [27, 28] report the green synthesis of 1-pyridyl imidazo[1,5-a]pyridines at room temperature in the presence of ionic liquid.

However these methods require prolong and exotic reaction condition. Thus the development of a new method for the synthesis of imidazoles derivatives would be highly desirable. Here we report an easy procedure for synthesizing of 2-phenylimidazo [4,5-*f*] [1,10]-phenanthroline in the presence $[HBim]BF_4$ and ammonium acetate under solvent free condition with excellent yield and easy work up.

2. MATERIAL AND METHODS

2.1. Synthesis of 2-phenylimidazo [4,5-*f*] [1,10]-phenanthroline

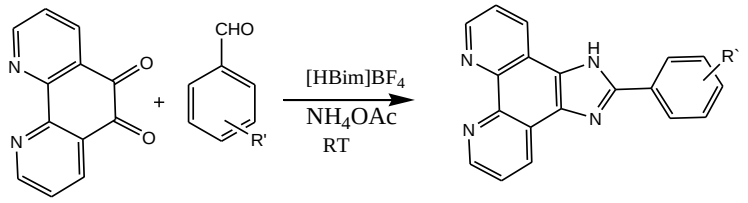
A mixture of benzaldehyde (1mmol)1,10-phenanthroline-5,6-dione,(1mmol),NH_4OAC(2.5mmol) and $[HBim]BF_4$ (10mmol) were ground together in a mortar with a pestle at room temperature for appropriate time as shown in table-1. Completion of reaction is confirmed by TLC the mixture was further purified by column chromatography by using methanol:benzene and recrystallized from methanol.

Many of the synthetic protocols for imidazo derivatives reported so far suffer from one or more disadvantages such as harsh reaction condition, poor yield, prolong reaction times, or use of hazardous and often expensive catalysts.

Recently ionic liquid has received considerable attention as an inexpensive, nontoxic, readily available catalyst for various organic transformation [29] offering the corresponding products in excellent yield with high selectivity. The mild Lewis acidity associated with ionic liquid enhanced its usage in organic synthesis to realize several organic transformation using stioichiometric levels to catalytic amount. Owing to numerous advantages associated with this eco-friendly element, ionic liquid has been explored as a powerful catalyst for various organic transformations. During the course of our studies towards the development of new routes to the synthesis of biologically active heterocycles the ammonium acetate is acting as a nitrogen source for the formation of imines I. Due to the high selectivity the [HBim]BF4 ionic liquid attached to the both carbonyl group of 1,10-phenanthroline give an intermediate II which cyclized to form product via intermediate III as mention in scheme-2.

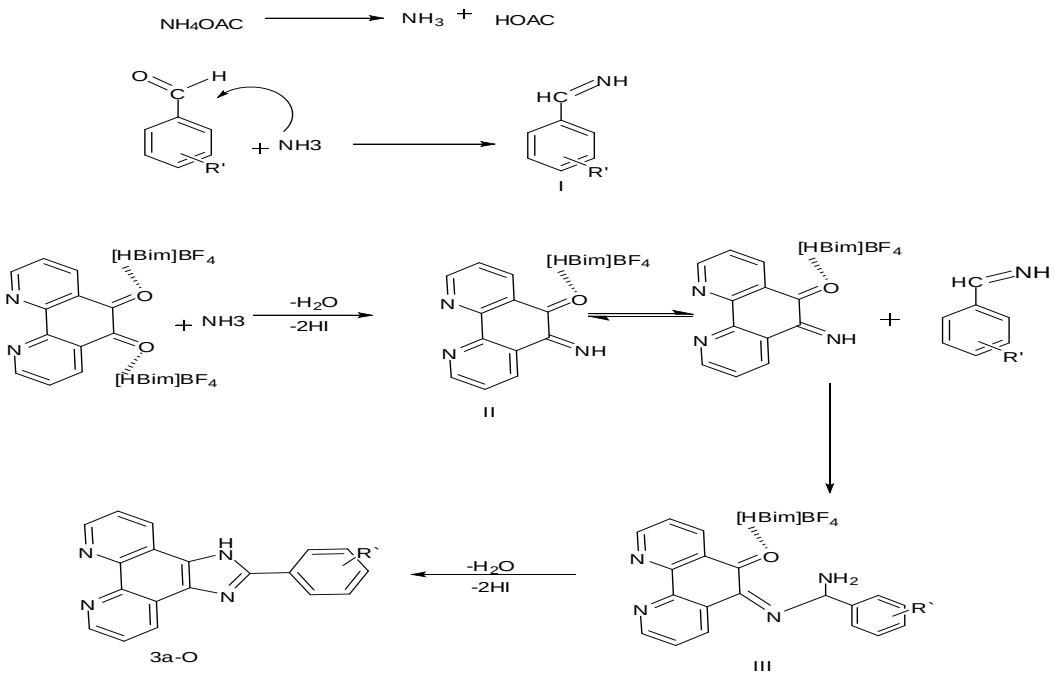
By getting this result, we have extended this protocol to a variety of aldehydes and summarized in Table 1. This protocol is rapid and efficient for the preparation of several2-phenylimidazo [4,5-*f*] [1,10]-phenanthroline from both electrons efficient as well as electron deficient aromatic aldehydes. Electron-withdrawing groups enhance the rate of the reaction as compare to the electron-donating group. Aliphatic aldehydes were also used as starting carbonyl compounds for the same reaction. The *ortho* and *para* substituents activate the aromatic ring of aldehydes and increase the rate of the reaction. While *meta* substitution requires somewhat greater time as compared to the *o/p* substituents. A nearly stiochiometric amount of ammonium acetate was used in the course of the reaction, whereas previously a many-fold excess of ammonium acetate was required. This is an additional advantage of the novel methodology.

Here we report an easy procedure for synthesizing of 2-phenylimidazo [4,5-*f*] [1,10]-phenanthroline catalyzed by inexpensive, easily available and nontoxic [HBim]BF_4 in the presence of ammonium acetate under solvent free condition with excellent yield and easy work up.



1 2 3a-o

Scheme-1

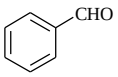
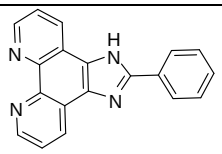
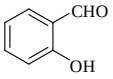
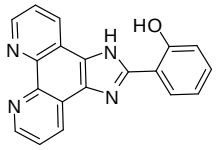
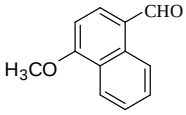
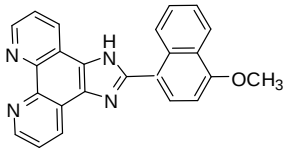
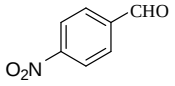
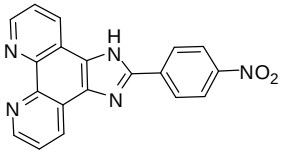
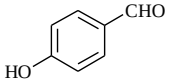
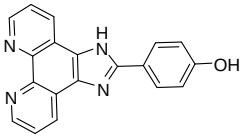
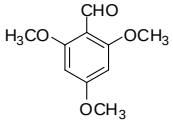
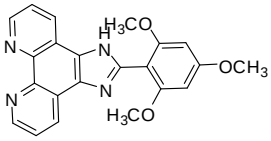
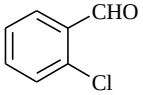
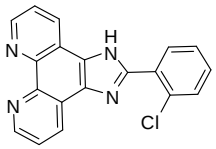
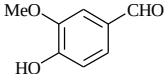
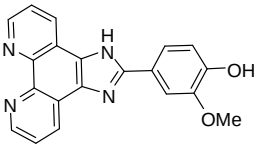


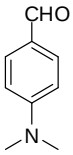
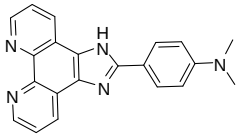
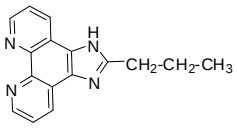
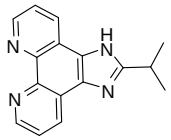
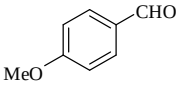
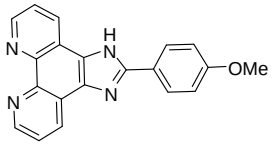
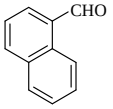
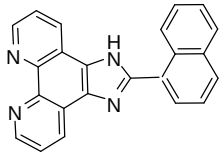
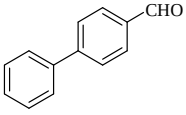
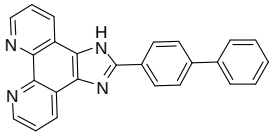
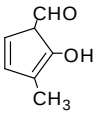
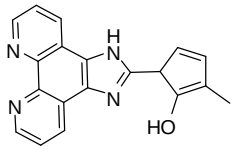
Scheme-2 Possible mechanism of the synthesis of 3a-m

3. RESULT AND DISCUSSION

In conclusion, molecular iodine was found to be a mild and effective catalyst for the formation of 2-phenylimidazo [4,5-*f*] [1,10]-phenanthroline in excellent yields. The uses of this inexpensive and easily available catalyst under solvent-free conditions make this protocol practical and economically attractive. The simple work-up procedure, mild reaction conditions, selectivity, and very good yields make our methodology a valid contribution to the existing processes in the field of 2-phenylimidazo [4,5-*f*] [1,10]-phenanthroline derivatives synthesis.

The formation of 2-phenylimidazo [4,5-*f*] [1,10]-phenanthroline are confirmed by spectral analysis. The IR spectra of 4-N,N-dimethyl-2-phenylimidazo [4,5-*f*] [1,10]-phenanthroline shows absorption at 1687,2257 and 3355cm^{-1} corresponding to the C=N, NH and tertiary amino group respectively. The ^{1}HNMR spectra shows 1H(s) δ=2.0,for NH gr, 6H(s) δ=3.00 for methyl group,4H(d) δ=6.65-7.30for aromatic benzene, 4H(d) δ=8.00-8.81,2(H) δ=7.26 mass 207(M^{+}),185,165,127. These result shows the confirmation of the formation 4-N,N-dimethyl-2-phenylimidazo [4,5-*f*] [1,10]-phenanthroline(3i).

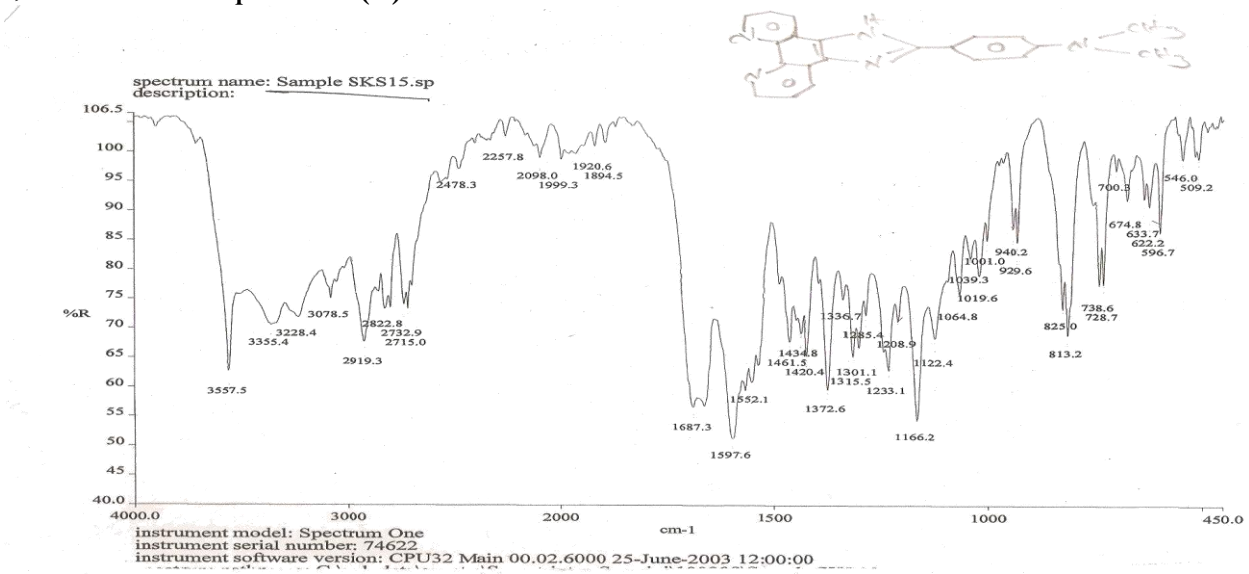
Entry	Aldehyde	Product	Time(sec).	Yield (%)
3a			18	80
3b			20	90
3c			16	89
3d			10	80
3e			14	88
3f			15	90
3g			20	89
3h			17	93

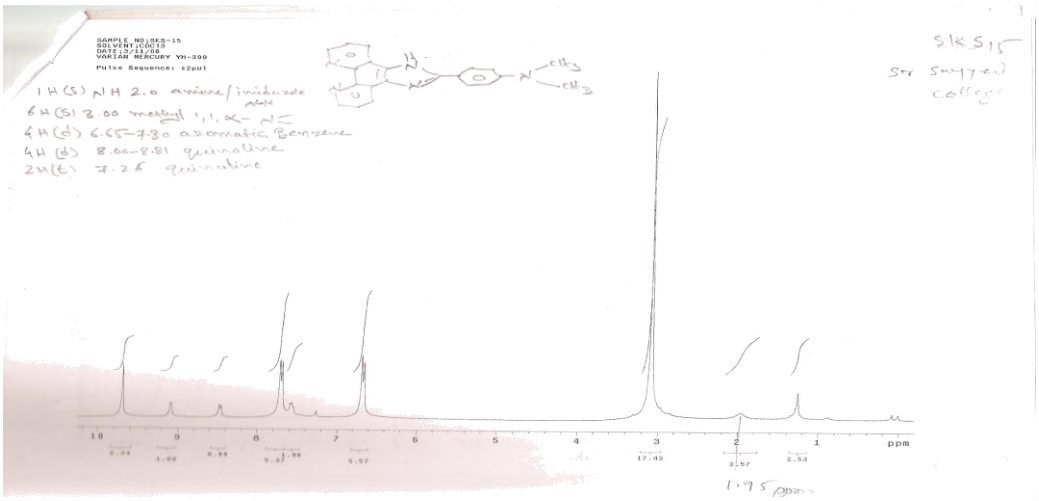
3i			15	83
3j	CH_3-CH_2-CH_2-CHO		25	80
3k			30	85
3l			18	92
3m			25	86
3n			30	78
3o			24	87

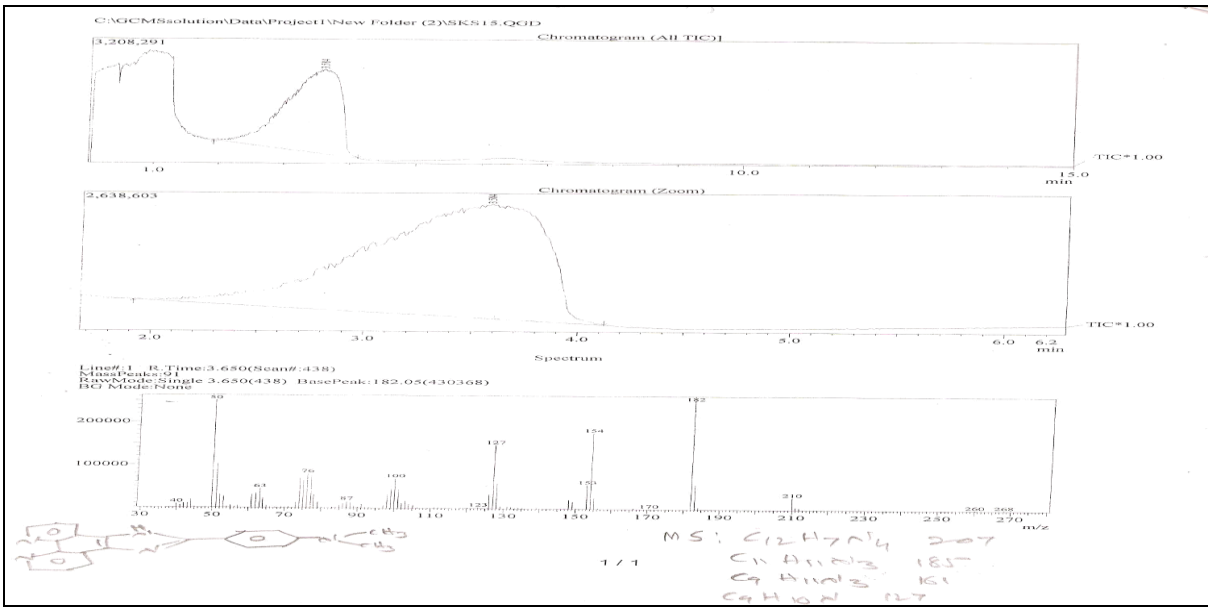
[a]*Products were characterized by* ^{1}H *NMR,* ^{13}C *NMR, Mass, elemental analysis and comparison with authentic sample,*
[b]*Isolated yield after column chromatography.*

Spectra of some compound:

1.IR , NMR and Mass Spectra of (3i):







General procedure for the synthesis of 2-phenylimidazo [4,5-*f*] [1,10]-phenanthroline(3a-o):

A mixture of benzaldehyde(1mmol), 1,10-phenanthroline 5,6-dione(1mmol), ammonium acetate (20mmol) and $[HBim]BF_4$ (10mmol) were grind together in a mortar with pestle at room temperature for appropriate time **Table-1** after completion of reaction confirmed by TLC . The crude was further purified by column chromatography by using petroleum ether: ethyl acetate (9:1) eluent and get the corresponding 2-phenylimidazo [4,5-*f*] [1,10]-phenanthroline **.** The products **3(a-o)** were confirmed by comparison with authentic sample, ^1H NMR, ^{13}C NMR, mass, elemental analysis and melting points.

4. ACKNOWLEDGMENT

Author thankful to Dr. Shaikh Kabeer Ahmed principal of Sir Sayyed college Aurangabad for valuable guidance and also thankful to department of chemistry, B.Raghunath college, Parbhani.

5. REFERENCES

1. Donoghue KA, Kelly JM, Kruger PE. *Dalton Trans*.2004; **1**.
2. Metcalfe,C.;Thomas,J.A.;*Chem.Soc.Rev*.2003;**32**:215
3. Tan LF, Chao H, Liu YJ, Sun B, Wei W Ji. *L. N*. 2005; **13**:4693.
4. Biachi G, Rodrigues A,Yakurshigiu K.*J.Org.Chem* 1989;**54**:4497.
5. Bolger L,Brittain RJ, Jack D,Jackson MR, Martin LE, Mills J, Poynter D, Tyers MB.*Nature(London)*1972;**238**:354.
6. ZitoSW, MartlnezMJ, *Biol.chem*1980; **225**:8645.

7. Jansonius JN, Eichele G, Ford GC, Picot D, Thaller C, Vicent MG, In Transaminases; Christen P, Metzler DE. *Eds Wiley:NewYork*, 1985; **110**.
8. Arbilla S, Allen J, Wick A, Langer S. *Eur. J. Pharmacol*. 1986; **130**:257.
9. Ford NF, Browne LJ, Campbell T, Gemenden C, Goldstein R,Gude C, Wasley JNF.*J.Med.Chem*.1985;**28**:164.
10. Ligtenbarg AJ, Spek AL, Hage R, Feringa BL. *J. Chem. Soc. DaltonTrans*.1999; 659.
11. Bluhm ME, Ciesielski M, Gorls H, Walter O, Doring M.*Inorg.Chem*.2003;**42**:8878.
12. Steck E A, Day AR, *J.Am.Chem.Soc*.1943;**65**:452
13. MichaelGB,Derek AT, Kiranmoy C,Shubhamoy C, Dipankar D, *New.J.Chem.* 2004; **28**:32-32.
14. Arshia Parveen.,Sk Md Rafi,Shaikh.Kabeer A, Deshmukh SP, PawarRP. *ARKIVO.*2007**; 14:**12-18.
15. (a)Bower JD, Ramage GR. *J. Chem. Soc*. 1955: 2834. (b)Winterfeld K, Franzke H, *Angew. Chem. Int. Ed. engl.* 1963; **75**:1101.
16. (a) BourdaisJ,Omar A. M. E. *J. Heterocycl. Chem*.1980**; 17**:555. (b)ElKhadem HS, Kawai J, Sartz DL.*Hetrocycles.*1989; **28**:239
17. SasakiK,TsurumoriA,HirotaT. *J. Chem. Soc. Perkin Trans.* 1998; 3851.
18. PalaciosF, Alonso C,Rubiales G.*Tetrahedron.*1995;**51**:3683.
19. KartritzkyAR,QiuG. *J. Org. Chem*.2001; 662862.
20. (a)Krapcho AP, Powell JR. *Tetrahedron Lett.* 1986; **27**:3713. (b)Grigg R, Kennewell P,Savic V, SridharanV. *Tetrahedron.*1992; **48**:10423.
21. WangJ, DyersL, MasonR. Jr, Amoyaw PJr, BuXR. *J. ORG. Chem*. 2005; **70**:2353.
22. Bluhm ME, Ciesielski M, Gorls H, Walter O, Doring M. *Angew. Chem. Int. Ed*. 2002; **41**:2962.
23. Radziszeski B, *Chem.Ber*.1882; **15**:1493.
24. Japp FR, Robinson HH,*Chem Ber*,1882;**15**:1268.
25. Grimmett MR, *Pergamon: New York.* 1996; **3**:77.
26. Shahed Ali *Arch.Appl.Sci.Res*.2010; **2 (5)**: 397
27. a)Siddiqui SA, Potewar TM, Lahoti R J,Srinivasan KV.*Synthesis.* 2006;2849. b)Bhosale RS, Sarda SR, Ardhapure SS, Jadhav WN, Bhusare SR, Pawar RP.*Tetrahedron Letters*, 2005; **46**:7183.
28. Jarikote DV, Siddiqui SA,Rajgopal R,Thomas D,Lahoti RJ , Srinivasan KV. *Tetrahedron Lett***,** 2003; **44**:1835.
29. a) Rajgopal R, Jarikote DV, Lahoti RJ, Thomas D, Srinivasan KV.*Tetrahedron Lett*. 2003;**44**:1615; b)Gholap AR, Venkatesan K, Thomas D, Lahoti RJ Srinivasan KV. *Green Chem*, 2004; **6**:147-150. c)Panchgalle SP, Kalkote UR, Nipahadkar PS, Joshi PN, Chavan SP, Chaphekar GM, *Green Chem*. 2004; **6:** 308-309.