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Ionic liquid catalyzed multicomponent synthesis of 3,4-dihydro-3-substituted-2*H*-naphtho[2,1-*e*][1,3]oxazine derivatives

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Abstract: An efficient and novel one-pot synthesis of 3,4-dihydro-3-substituted-2*H*-naphtho[2,1-*e*][1,3]oxazine derivatives from 1-naphthol, various anilines and formalin at room temperature stirring. The six-membered N,O-heterocyclic skeleton was constructed via 1-benzyl-3-methyl imidazolium hydrogen sulphate [bnmim] [HSO_4] promoted Mannich type reaction.

Keywords: 1,3-oxazines; ionic liquid; Mannich type reaction; multicomponent reaction.

1. Introduction

Multicomponent reactions (MCRs), defined as one pot reactions in which at least three functional groups join through covalent bonds, have been steadily gaining importance in synthetic organic chemistry.[1-4] The reagents employed may be different molecules or they may be different molecules or they may be different functional groups of the same reagent. Speed, diversity, efficiency and environmental amiability are some of the key features of this class of reactions. Ionic liquids (ILs) have aroused considerable interest over the past decade due to their wide variety of properties. In this regard, they can be used as solvents and reaction supports.[5-8] They exist in liquid state at ambient temperature; hence the reactions in presence of ILs need no additional solvent. Ionic liquids have attracted much attention due to their mild reaction conditions, short reaction times and better yield, solvating ability and easy recyclability.[9-11] Various reactions have been reported recently using ionic liquid as a catalyst, reaction media.[12, 13]

The Mannich reaction has been widely used[14-16] to introduce oxazines into a variety of organic compounds. The Mannich reaction involving phenols, formalin and primary amines has been used as a convenient source for a variety of compounds. The 1,3 Oxazine nucleus features prominently in many biologically important natural products[4] and other bioactive molecules.[18-21] The most outstanding of these is Sustiva (Efavirenz), a non-nucleoside reverse transcriptase inhibitor that has been approved by the FDA in 1998 and is presently in clinical use for the treatment of AIDS.[21] This has been the prime

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driving force for the synthesis of various compounds incorporating the 1,3-oxazine moiety. In addition, naphthoxazine derivatives have exhibited therapeutic potential for the treatment of Parkinson's disease.[22, 23]

Although several methods for the preparation of 1,3-oxazine derivatives have previously been reported,[24-26] few have been focused on the multicomponent reactions method. The present method is beneficial over previous reports due to its solvent-free condition. As per our interest[27-29] to develop better protocols for the synthesis of biologically active heterocyclic molecules, we would like to report the synthesis of a series of 3,4-dihydro-3-substituted-2*H*-naphtho[2,1-*e*][1,3]oxazine derivatives using 1-naphthol, formalin and anilines as substrates in presence of 1-benzyl-3-methyl imidazolium hydrogen sulphate [bnmim] [HSO_4], ionic liquid as a catalyst.

2. Results and Discussion

Herein, we wish to report the synthesis of 3,4-dihydro-3-substituted-2*H*-naphtho[2,1-*e*][1,3]oxazine derivatives promoted by ionic liquid as a catalyst (Scheme 1). We have considered the reaction of aniline (1 mmol), 1-naphthol (1 mmol) and formalin (2 mmol) under room temperature stirring condition as the model reaction.

To optimize the reaction conditions in order to evaluate the effect of acidic ionic liquids such as 1-methylimidazolium hydrogen sulfate i.e. [hmin] [HSO_4], 1-ethylimidazolium hydrogen sulfate i.e. [heim] [HSO_4] and 1-benzyl-3-methyl imidazolium hydrogen sulfate i.e. [bnmim] [HSO_4] screened for the model reaction (Table 1). The results indicate that [bnmim][HSO_4] catalyst gave the good result to form the desired product in 77 % yield within 1 min (Table 1, entry 3).

To study the concentration of catalyst loading for model reaction, the procedure was optimized using different molar concentrations of [bnmim] [HSO_4] under room temperature stirring condition. High yield of product **4a** was observed using 40 mol% of catalyst while with 10-30 mol% of catalyst yields were not good (Table 2). From these results, it was evident that, the concentration of catalyst plays a crucial role to improve the result to greater extent. It was also observed that, there is no greater change in yields of product greater than 40 mol% of catalyst.

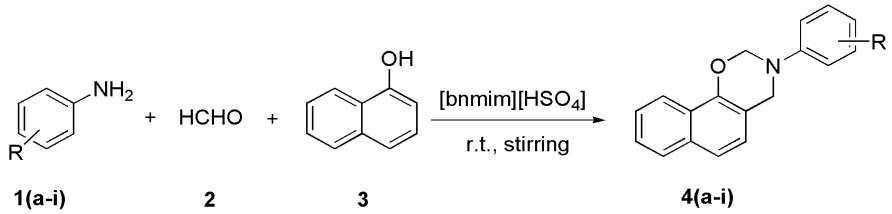
To explore, the generality and scope of this method a wide variety of substituted aromatic anilines were reacted with the formalin and 1-naphthol under the same experimental conditions to afford the corresponding 3,4-dihydro-3-substituted-2*H*-naphtho[2,1-*e*][1,3]oxazine derivatives. 1-Benzyl-3-methyl imidazolium hydrogen sulphate [bnmim] [HSO_4] was found to be compatible with various substituents (electron withdrawing as well as donating substituents) such as OMe, OEt, Me, F and Br. The resultant products were obtained in good to excellent yields in short reaction times (Table 3) (Scheme 1).

The ^{1}H NMR spectra of compounds **(4a-i)** showed typical two singlet peaks in the region 4.52-4.90 ppm and 5.40-5.70 ppm, which are due to protons of –Ar-CH_2-N- and –O-CH_2-N- of oxazine ring respectively.

3. Conclusion

In conclusion, [bnmim] [HSO_4] as a catalyst used can readily be recycled. It can be used repeatedly for several times without appreciable loss in activity. The method is advantageous due to high conversion, short reaction time, clean reaction profile, simple experimental and workup procedures for the synthesis of (4a-i) compounds.

Multicomponent synthesis of oxazine derivatives



Scheme 1. Reaction of various anilines with formalin and 1-naphthol.

Table 1. Effect of different acidic ionic liquids on synthesis of **4a**.

Entry	Ionic liquid	Time (min)	Yield (%)
1	[hmin] [HSO_4]	1.0	58
2	[heim] [HSO_4]	1.0	63
3	[bnmim][HSO_4]	1.0	77

Reaction Conditions: [a]Formalin (2.0 mmol), aniline (1.0 mmol), 1-naphthol (1.0 mmol), catalyst (40 mol%), r.t., grinding. [b]Isolated yields

Table 2. Effect of catalyst loading on the one-pot, three component synthesis of **4a**[a].

Entry	[bnmim] [HSO_4] mol%	Time (min)	Yield (%)[b]
1	10	10.0	38
2	20	6.0	46
3	30	3.5	52
4	40	1.0	77
5	50	1.0	77
6	60	1.0	77

Reaction Conditions: [a]Formalin (2.0 mmol), aniline (1.0 mmol), 1-naphthol (1.0 mmol), r.t., stirring. [b]Isolated yields.

Table 3. Reaction of various anilines with 1-naphthol and formalin (1:1:2).

Entry	Compound	R	Time (min)	Yield (%)[a]	M. P. (°C)
1	4a	H	1.0	77	62-63[b]
2	4b	4-OMe	1.0	61	300 (d)
3	4c	4-OEt	1.0	58	76-77
4	4d	2,4,6-Tri Br	1.5	75	72-74
5	4e	4-Me	2.0	60	196-198
6	4f	2-OEt	1.0	71	200(d)
7	4g	4-F	1.5	68	118-120
8	4h	3-OMe	1.0	67	280(d)
9	4i	2-Me	1.0	65	86-88

[a]Isolated yield.

4. Experimental

All chemicals and solvents were purchased from Merck, Spectrochem, Lancaster and S. D. Fine-chem. (India). Melting points were determined in open capillaries on Kumar's melting point apparatus (India) and are uncorrected. IR spectra were recorded on JASCO FT-IR 4100, Japan using KBr discs. ^{1}HNMR spectra were recorded on Varian NMR spectrometer, Model Mercury Plus (400 MHz), Mass spectra [ES-MS] were recorded on a Water-Micro mass Quattro-II spectrophotometer. Elemental analyses were performed on CHNS analyzer Flash 1112, Thermo Finnigan. The progress of the reactions was monitored by TLC on Merck silica plates. Results are presented as, chemical shift δ in ppm. Multiplicities are shown as the abbreviations: s (singlet), t (triplet), q (quartet), m (multiplet). Solvents were commercially available materials of reagent grade.

4.1 General procedure for the synthesis of compounds (4a-i):

A mixture of formalin (2.0 mmol), aromatic amine (1.0 mmol), 1-naphthol (1.0 mmol) and [bnmim] [HSO_4] (40 mol%) was stirred at room temperature. The progress of the reaction was monitored on TLC. After completion of reaction, reaction mixture was extracted with methylene dichloride (3×50 mL) and the insoluble ionic liquid [bnmim] [HSO_4] directly recycled in subsequent runs. The organic layer was washed with water (2×10 mL) and brine (2×20 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The obtained crude product was purified by column chromatography on silica gel by hexane: ethyl acetate as an eluent.

4.2 Spectral data of principle compounds:

3,4-dihydro-3-phenyl-2H-naphtho[2,1-e][1,3]oxazine (4a). IR (KBr, ν_{max}/cm^{-1}): 1030 (sym.C-O-C), 1214 (asym. C-O-C); ^{1}H NMR (DMSO-d_6, 400 MHz, δ ppm): 4.77 (s, 2H, -Ar-CH_2-N-), 5.41 (s, 2H, -O-CH_2-N-), 6.82-7.56 (m, 11H, Ar-H); ^{13}C NMR (DMSO-d_6, 75 MHz,, δ ppm): 49.1, 79.4, 112.7, 115.3, 117.5, 119.8, 120.7, 124.2, 125.2, 125.5, 126.0, 127.6, 129.2, 132.9, 147.9, 148.8; MS: m/z 262.2 (m+1); Elemental analysis: $C_{18}H_{15}NO$ Calcd.: C: 82.73%; H: 5.79%; N: 5.36%; Found: C: 82.65%, H: 5.83%, N: 5.48%.

3,4-dihydro-3-(4-methoxyphenyl)-2*H*-naphtho[2,1-e][1,3]oxazine (4b). IR (KBr, ν_{max}/cm^{-1}): 1019 (sym.C-O-C), 1228 (asym. C-O-C); ^{1}H NMR (DMSO-d_6, 400 MHz, δ ppm): 3.62 (s, 3H, OMe), 4.87 (s, 2H, -Ar-CH_2-N-), 5.40 (s, 2H, -O-CH_2-N-), 6.77-7.82 (m, 10H, Ar-H); ^{13}C NMR (DMSO-d_6, 75 MHz,, δ ppm): 48.2, 52.2, 80.1, 111.2, 115.6, 117.4, 119.5, 121.1, 124.2, 125.7, 125.9, 126.8, 127.2, 130.1, 132.3, 146.8, 148.6; MS: m/z 292.2 (m+1); Elemental analysis: $C_{19}H_{17}NO_2$ Calcd.: C: 78.33 %; H: 5.88 %; N: 4.81 %; Found: C: 78.45%, H: 5.90%, N: 4.72%.

3-(4-ethoxyphenyl)-3,4-dihydro-2*H*-naphtho[2,1-e][1,3]oxazine (4c). IR (KBr, ν_{max}/cm^{-1}): 1028 (sym.C-O-C), 1224 (asym. C-O-C);^{1}H NMR (DMSO-d_6, 400 MHz, δ ppm): 1.20 (t, 3H, J = 8 Hz, O-CH_2-$\underline{CH_3}$), 3.90 (q, 2H, J = 8 Hz ,O-$\underline{CH_2}$-CH_3), 4.90 (s, 2H, -Ar-CH_2-N-), 5.40 (s, 2H, -O-CH_2-N-), 6.80-7.80 (m, 10H, Ar-H); ^{13}C NMR (DMSO-d_6, 75 MHz,, δ ppm): 14.6, 48.4, 65.1, 80.6, 112.6, 115.9, 117.4, 119.7, 120.1, 123.4, 124.8, 125.2, 125.8, 126.5, 127.7, 129.8, 132.0, 147.2; MS: m/z 306.2 (m+1); Elemental analysis: $C_{20}H_{19}NO_2$ Calcd.: C: 78.66%; H: 6.27%; N: 4.59%; Found: C: 78.71%, H: 6.28%, N: 4.24%.

3-(2,4,6-tribromophenyl)-3,4-dihydro-2H-naphtho[2,1-e][1,3]oxazine (4d). IR (KBr, ν_{max}/cm^{-1}): 1016 (sym.C-O-C), 1224 (asym. C-O-C); ^{1}H NMR (DMSO-d_6, 400 MHz, δ ppm): 4.52 (s, 2H, -Ar-CH_2-N-), 5.53 (s, 2H, -O-CH_2-N-), 6.86-7.92 (m, 8H, Ar-H); ^{13}C NMR (DMSO-d_6, 75 MHz,, δ ppm): 50.2, 79.3, 106.5, 107.9, 119.5, 124.7, 125.4, 125.9, 126.4, 127.2, 132.6, 133.5, 134.9, 142.6, 147.2, 150.1; MS: m/z 495.1 (m+1); Elemental analysis: $C_{18}H_{12}Br_3NO$ Calcd.: C: 43.41%; H: 2.43%; N: 2.81%; Found: C: 43.58%, H: 2.25%, N: 2.64%.

3,4-dihydro-3-*p*-tolyl-2*H*-naphtho[2,1-e][1,3]oxazine (4e). IR (KBr, ν_{max}/cm^{-1}): 1021 (sym.C-O-C), 1234 (asym. C-O-C); ^{1}H NMR (DMSO-d_6, 400 MHz, δ ppm): 2.40 (s, 3H, CH_3), 4.90 (s, 2H, -Ar-CH_2-N-), 5.60 (s, 2H, -O-CH_2-N-), 6.60-7.90 (m, 10H, Ar-H); ^{13}C NMR (DMSO-d_6, 75 MHz,, δ ppm): 21.2, 49.2, 78.8, 110.4, 115.2, 117.8, 119.6, 120.3, 124.5, 125.5, 125.9, 126.3, 127.4, 129.6, 132.1, 147.8, 148.2; MS: m/z 276.2 (m+1); Elemental analysis: $C_{19}H_{17}NO$ Calcd.: C: 82.88%; H: 6.22%; N: 5.09%; Found: C: 82.71%, H: 6.30%, N: 5.04%.

3-(2-ethoxyphenyl)-3,4-dihydro-2H-naphtho[2,1-e][1,3]oxazine(4f). IR (KBr, ν_{max}/cm^{-1}): 1021 (sym.C-O-C), 1234 (asym. C-O-C); ^{1}H NMR (DMSO-d_6, 400 MHz, δ ppm): 1.29 (t, 3H, J = 14 Hz, O-CH_2-$\underline{CH_3}$), 3.96 (q, 2H, J = 14 Hz ,O-$\underline{CH_2}$-CH_3), 4.61 (s, 2H, -Ar-CH_2-N-), 5.40 (s, 2H, -O-CH_2-N-), 6.17-7.44 (m, 10H, Ar-H); ^{13}C NMR (DMSO-d_6, 75 MHz,, δ ppm): 13.9, 48.8, 64.7, 81.5, 111.8, 114.7, 115.8, 117.5, 118.6, 121.2, 122.2, 124.5, 125.4, 125.7, 126.2, 127.4, 128.8, 133.2, 146.1, 149.3; MS: m/z 306.2 (m+1); Elemental analysis: $C_{20}H_{19}NO_2$ Calcd.: C: 78.66%; H: 6.27%; N: 4.59%; Found: C: 78.48%, H: 6.37%, N: 4.67%.

3-(4-fluorophenyl)-3,4-dihydro-2*H*-naphtho[2,1-e][1,3]oxazine (4g). IR (KBr, ν_{max}/cm^{-1}): 1026 (sym.C-O-C), 1245 (asym. C-O-C);^{1}H NMR (DMSO-d_6, 400 MHz, δ ppm): 4.90 (s, 2H, -Ar-CH_2-N-), 5.60 (s, 2H, -O-CH_2-N-), 6.80-7.80 (m, 10H, Ar-H); ^{13}C NMR (DMSO-d_6, 75 MHz,, δ ppm): 49.2, 78.5, 112.2, 115.7, 116.1, 117.2, 118.2, 122.4, 123.1, 125.1, 125.6, 125.9, 127.5, 128.4, 130.4, 150.2 ; MS: m/z 280.2 (m+1); Elemental analysis: $C_{18}H_{14}FNO$ Calcd.: C: 77.40%; H: 5.05%; N: 5.01%; Found: C: 77.87%, H: 5.14%, N: 5.15%.

3,4-dihydro-3-(3-methoxyphenyl)-2H-naphtho[2,1-e][1,3]oxazine (4h). IR (KBr, ν_{max}/cm^{-1}): 1029 (sym.C-O-C), 1211 (asym. C-O-C); ^{1}H NMR (DMSO-d_6, 400 MHz, δ ppm): 3.54 (s, 3H, OMe), 4.70 (s, 2H, -Ar-CH_2-N-), 5.50 (s, 2H, -O-CH_2-N-), 6.21-7.63 (m, 10H, Ar-H); ^{13}C NMR (DMSO-d_6, 75 MHz, δ ppm): 49.1, 53.4, 79.2, 112.1, 114.5, 115.8, 117.3, 118.2, 120.9, 124.5, 125.6, 125.9, 126.5, 127.5, 130.3, 133.1, 146.7, 148.9, 151.1; MS: m/z 292.2 (m+1); Elemental analysis: $C_{19}H_{17}NO_2$ Calcd.: C: 78.33 %; H: 5.88 %; N: 4.81 %; Found: C: 78.21%, H: 5.78%, N: 4.90%.

3,4-dihydro-3-*o*-tolyl-2*H*-naphtho[2,1-e][1,3]oxazine (4i). IR (KBr, ν_{max}/cm^{-1}): 1029 (sym.C-O-C), 1231 (asym. C-O-C); ^{1}H NMR (DMSO-d_6, 400 MHz, δ ppm): 2.20 (q, 3H, CH_3), 4.90 (s, 2H, -Ar-CH_2-N-), 5.70 (s, 2H, -O-CH_2-N-), 6.80-7.90 (m, 10H, Ar-H); ^{13}C NMR (DMSO-d_6, 75 MHz,, δ ppm): 20.2, 50.1, 79.1, 113.2, 116.1, 117.4, 119.2, 120.5, 124.7, 125.8, 126.1, 126.8, 127.9, 129.7, 130.4, 147.2, 148.1, 149.2, 150.4; MS: m/z 276.2 (m+1); Elemental analysis: $C_{19}H_{17}NO$ Calcd.: C: 82.88%; H: 6.22%; N: 5.09%; Found: C: 82.84%, H: 6.68%, N: 5.14%.

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References

[1] Toure, B. B.; Hall, D. G. Natural product synthesis using multicomponent reaction strategies. *Chem. Rev.* **2009**, *109*, 4439-4486.

[2] Bondock, S.; Fadaly, W.; Metwally, M. A. Recent trends in the chemistry of 2-aminobenzothiazoles. *J. Sulfur Chem.* **2009**, *30*, 74-107.

[3] Ganem, B. Strategies for innovation in multicomponent reaction design. *Acc. Chem. Res.* **2009**, *42*, 463-472.

[4] Domling, A.. Recent developments in isocyanide based multicomponent reactions in applied chemistry .*Chem. Rev.* **2006**, *106*, 17-89.

[5] Shelke, K. F.; Madje, B. R.; Sapkal, S. B.; Shingate, B. B.; Shingare, M. S. An efficient ionic liquid promoted Knoevenagel condensation of 4-oxo-4*H*-benzopyran-3-carbaldehyde with Meldrum's acid. *Green Chem. Lett. Rev*. **2009**, *2*, 3-7.

[6] Sadaphal S. A.; Shelke, K. F.; Sonar, S. S.; Shingare, M. S. Ionic liquid promoted synthesis of Bis(indolyl)methanes. *Central Euro. J. Chem.*, **2008**, *6*, 622-626.

[7] Shelke, K. F., Sapkal, S. B., Shitole, N. V., Shingate, B. B., Shingare, M, S. Microwave-assisted synthesis of 1,2-benzisoxazole derivatives in ionic liquid. *Org. Commun*. **2009**, 2, 72-78.

[8] Murugesan, S.; Linhardt, R. J. Ionic Liquids in carbohydrate chemistry: Current trends and future directions. *Curr. Org. Synth.* **2005**, *2*, 437-451.

[9] Welton, T. Room-temperature ionic liquids: Solvents for synthesis and catalysis *Chem. Rev.* **1999**, *99*, 2071-2084.

[10] Wassercheid, P.; Keim, W. Ionic liquids: New solutions for transition metal catalysis. *Angew. Chem. Int. Ed.* **2000**, *39*, 3772-3789.

[11] Sheldon, R. Catalytic reactions in ionic liquids. *Chem. Commun.* **2001**, 2399-2407.

[12] Sadaphal, S. A.; Sonar, S. S.; Kategaonkar, A. H.; Shingare, M. S. 1-Benzyl-3-methyl imidazolium hydrogen sulphate [bnmim][HSO_4] promoted synthesis of α-aminophosphonates. *Bull. Korean Chem. Soc.***2009**, *30*, 1054-1056.

[13] Panchgalle, S. P.; Kalkote, U. R.; Niphadkar, P. S.; Joshi, P. N.; Chavan, S. P.; Chaphekar, G. M. Sn-β molecular sieve catalyzed Baeyer-Villiger oxidation in ionic liquid at room temperature. *Green Chem.* **2004**, *6*, 308-309.

[14] Reichert, B. Die Mannich reaction; Springer-Verlag: Berlin, 1959.

[15] Blicke, F. F. Mannich reaction. *Org. Reactions* **1942**, *1*, 303-341.

[16] Hellmann, H.; Opitz, G. α-Aminoalkylierung; Verlag Chemie: Weinheim, 1960.

[17] Corey, E. J.; Cheng, X. M. The logic of chemical synthesis; John Wiley and Sons: New York, NY, 1989; 423.

[18] Kobayashi, M.; Kitazawa, M.; Sotio, T.; Yamamoto, R.; Harada, H. Studies on the synthesis of antiulcer agents. II. Synthesis and antiulcer activity of cyclic carbamate derivatives. *Yakugaku Zasshi* **1984**, *104,* 659-679; *Chem. Abstr.* **1985**, *102*, 6344m.

[19] Testa, E.; Fontanella, L.; Cristiani, G.; Gallo, G. 5,5-Disubstituted dihydro-1,3-oxazine-2,4-diones. Research on compounds active on central nervous system XII. *J. Org. Chem.* **1959**, *24,* 1928-1936.

[20] Vrouenraets, S. M.; Wit, W. F.; van Tongeren, J.; Lange, J. M. Efavirenz: a review.*Expert. Opin. Phamacother*. **2007**, *8*, 851-871.

[21] Fauran, C. P.; Douzon, C.; Raynaud, G.; Sergant, M.; Novel derivatives of substituted tetrahydro M-oxazines, their process of preparation and their therapeutic application.. US 3,821,215, **1974**; *Chem. Abstr.* **1974,** *82*, 125412.

[22] Joyce, J. N.; Presgraves, S.; Renish, L.; Borwege, S.; Osredkar, T.; Hagner, D..; Replogle, M.; PazSoldan M.; Millan, M. J. Neuroprotective effects of the novel D3/D2 Receptor agonist and antiparkinson agent, S32504, in vitro against 1-methyl-4-phenylpyridinium (MPP+) and in vivo against 1-methyl-4-phenyl-1,2,3,6-tetrahydropyridine(MPTP): a comparison to ropinirole. *Exp. Neurol.* **2003**, *184*, 393-407.

[23] Kerdesky, F. A. J. A novel and efficient method for the conversion of a *trans*-hexahydronaphthoxazine to a *cis*- isomer using boron tribromide. *Tetrahedron Lett.* **2005**, *46*, 1711-1712.

[24] Agag, T. Preparation and properties of some thermosets derived from allyl-functional naphthoxazines. *J. App. Poly. Sci.* **2006**, *100*, 3769-3777.

[25] Burke W. J.; Murdock, K. C.; Ec, G. Condensation of hydroxyaromatic compounds with formaldehyde and primary aromatic amines. *J. Am. Chem. Soc.* **1954**, *76*, 1677-1679.

[26] Mathew, B. P.; Nath, M. One-pot three-component synthesis of dihydrobenzo- and naphtho[e]-1,3-oxazines in water. *J. Heterocyclic Chem.* **2009**, *46*, 1003-1006.

[27] Sapkal, S. B.; Shelke, K. F.; Shingate, B. B.; Shingare, M. S. Nickel nanoparticle catalyzed facile and efficient one-pot synthesis of polyhydroquinoline derivatives *via* Hantzsch condensation under solvent-free conditions. *Tetrahedron Lett.* **2009**, *50*, 1754-1756.

[28] Sonar, S. S.; Kategaonkar, A. H.; Ware, M. N.; Gill, C. H.; Shingate, B. B.; Shingare, M. S. Ammonium metavanadate: an effective catalyst for synthesis of α-hydroxyphosphonates. *Arkivoc* **2009**, *ii*, 138-148.

[29] Sonar, S. S.; Sadaphal, S. A.; Kategaonkar, A. H.; Pokalwar, R. U.; Shingate, B. B.; Shingare, M. S. Alum catalyzed simple and efficient synthesis of bis(indolyl)methanes by ultrasound approach. *Bull. Korean Chem. Soc.* **2009**, *30,* 825-828.