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Ultrasound-promoted solvent- and catalyst-free benzoylation of amines at room temperature: A green procedure

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ABSTRACT

A greener improvement to the *N*-benzoylation of amines, phenols and alcohols by benzoyl chloride was achieved using ultrasound irradiation without any solvent and catalyst. This simple, fast and highly efficient green procedure provided the products in high purity and quantitative yield within minutes at room temperature. This protocol does not require any water quenches, solvent separations and purification steps such as column chromatography or recrystallization.

KEYWORDS

N-benzoylation;
Amine;
Ultrasound irradiation;
Solvent-free;
Catalyst-free.

INTRODUCTION

Acylation of functional groups is a very useful reaction in the organic synthesis, especially in the synthesis of natural compounds and polyfunctional molecules such as nucleosides, carbohydrates, and steroids[1,2].

Amides have been extensively employed in the synthesis of industrial chemicals, drugs, polymers, agrochemicals, cosmetics and food additives[3]. Among the various developed synthetic methods, several reports are available in the literature for the synthesis of amides via acylation of amines with acyl donors such as acid chlorides, anhydrides, esters, acyl azides and carboxylic acids[4,5]. A number of synthetic methods have been reported in the literature for acylation of amines using acidic[6,7] or basic[8,9] conditions in organic media.

Earlier reported methods for the acylation of amines suffer from drawbacks such as the use of expensive and highly toxic, flammable or explosive reagents and various acid/basic catalysts which all destroyed and resulted in undesirable wastes and pollutants, problem in recovery of the large amount of soluble bases or acids, the environmental pollution caused by utilization of organic solvents, low yields, high temperatures, long reaction times, harsh reaction conditions, use of excess acylating agents, difficulty in availability or preparing the starting materials or catalysts, high cost and moisture-sensitivity of the catalysts, formation of undesirable or toxic by-products and purification through recrystallization or column chromatography. Therefore, development of mild, highly efficient and environmentally benign method for acylation of amines has been a major challenge in organic synthesis.

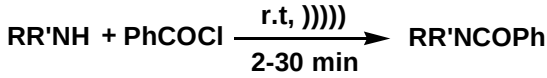
From the standpoint of 'green chemistry' and for reasons of economy and pollution, solvent-free methods are of great interest to make the classical procedures more clean, safe and easy to perform[10]. A catalyst-free and solvent-free procedure for the acylation of amines with acetic anhydride was also reported.[11,12] However; this procedure requires stirring of the reac-

tion mixture at relatively high temperature (80-85 °C), distillation or extraction for the separation of the products and column chromatographic for purification of the products.

Thus, development of an efficient, mild and convenient synthetic method for acylation of amines without any solvent, catalyst, bases, acids with high yields and pure products is an important subject.

Application of the ultrasound irradiation has received an increased attention in recent years and is able to activate several organic reactions[13,14]. A large number of organic synthesis can be carried out in higher yields, shorter reaction time and milder conditions under ultrasound irradiation than that of conventional methods. The sonication is used as an alternative energy source for the *N*-benzoylation of amines and involves high energies and pressures on an extremely short time scale. In an irradiated liquid, the collapse of bubbles caused by cavitation produces intense local heating and high pressures with very short lifetimes. These transient, localized hot spots can cause the reaction to take place rapidly. The hot spot has an equivalent temperature of roughly 5000 °C (9,000 °F), a pressure of about 2000 atmospheres, a lifetime considerably less than a microsecond and heating and cooling rates above 10 billion °C per second[13,14].

So, in continuation to our ongoing researches on the synthesis of nitrogen-containing compounds[15-17], we hereby report the *N*-benzoylation of amines by benzoyl chloride under solvent- and catalyst-free conditions using ultrasound irradiation (Scheme 1).



Scheme 1 : The *N*-benzoylation of amines under ultrasound irradiation

EXPERIMENTAL

Apparatus and analysis

All reagents were purchased from the Merck and Aldrich chemical companies and used without further purification. Products were characterized by comparison of their physical and spectral data with authentic samples. The NMR spectra were recorded in DMSO and $CDCl_3$. ^1H NMR spectra were recorded on a Bruker Avance DRX 90 MHz instrument. The chemical shifts (δ) are reported in ppm relative to TMS as an internal standard and *J* values are given in Hz. ^{13}C NMR spectra were recorded at 24.5 Hz. FT-IR (KBr) spectra were recorded on a Perkin-Elmer 781 spectrophotometer. Melting points were taken in open capillary tubes with a BUCHI 510 melting point apparatus and were uncorrected. The elemental analysis was performed using Heraeus CHN-O-Rapid analyzer. TLC was performed on silica gel polygram SIL G/UV 254 plates. Ultrasonication was performed in a PARSONIC 2600s ultrasound cleaner with a frequency of 28 kHz and an output power of 50 W (Builtin heating, 20-70 ºC thermo-statically adjustable). The reaction flask was located at the maximum energy area in the ultrasound cleaner, and the surface of the reactants was placed slightly lower than the level of water. The reaction temperature was controlled by addition or removal of water from the ultrasonic bath. The temperature of the water bath was controlled at about 25-30 °C.

Typical procedure for the N-benzoylation of amines

A mixture of benzoyl chloride (1 mmol) and amine (1 mmol) was irradiated by ultrasound for the appropriate time at room temperature (TABLE 1). During reaction a white crystalline solid separated out. After completion of the reaction (as monitored by TLC), the solid was separated and characterized by NMR, FT-IR and melting points. The physical data (mp, IR and NMR) of known compounds were found to be identical with those reported in the literature.[18-28] The formation of amides was confirmed by IR spectra, which showed two characteristic peaks (secondary NH and C=O). The ^1H NMR and ^{13}C NMR spectra of the amides showed one amide NH proton and carbonyl group signal, respectively.

^1H NMR spectra of selected compounds (90 MHz, acetone-d_6)

N-Phenylbenzamide (TABLE 1, entry 1): δ = 8.03-7.01 (m, 11H).

N-(2-Chlorophenyl) benzamide (TABLE 1, entry 2): δ = 8.99 (s, 1H), 8.25-7.12 (m, 9H).

N-(4-Nitrophenyl) benzamide (TABLE 1, entry 3): δ = 8.34-6.69 (m, 10H).

N-(2-Hydroxyphenyl)benzamide (TABLE 1, entry 4): δ = 9.45 (s, 1H), 9.22 (s, 1H), 8.13-6.83 (m, 9H).

N-(4-Hydroxyphenyl)benzamide (TABLE 1, entry 5): δ = 8.83 (s, 1H), 8.01-6.78 (m, 9H), 4.37 (s, 1H).

N-(3-Bromophenyl)benzamide (TABLE 1, entry 6): δ = 9.60 (s, 1H), 8.21-7.27 (m, 9H).

N-(2,6-Dimethylphenyl)benzamide (TABLE 1, entry 7): δ = 8.99 (s, 1H), 8.12-7.10 (m, 8H), 2.31 (s, 6H).

N-(2,4-Dimethylphenyl)benzamide (TABLE 1, entry 8): δ = 8.95 (s, 1H), 8.09-6.97 (m, 8H), 2.29 (s, 6H).

N-(4-Methoxyphenyl)benzamide (TABLE 1, entry 9): δ = 8.04-6.87 (m, 10H), 3.79 (s, 3H).

N-(2-Cyanophenyl)benzamide (TABLE 1, entry 10): δ = 9.60 (s, 1H), 8.12-7.32 (m, 9H).

N-Naphthalen-2-yl-benzamide (TABLE 1, entry 11): δ = 8.21-7.44 (m, 13H).

N-Benzylbenzamide (TABLE 1, entry 13): δ = 8.25 (s, 1H), 7.92-7.31 (m, 10H), 4.66 (s, 2H).

CAUTION

Although benzoyl chloride is often used as a source for acylation of functional groups, appropriate safety precautions should be taken.

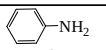
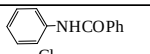
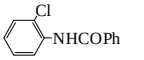
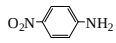
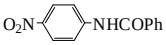
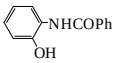
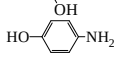
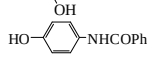
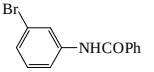
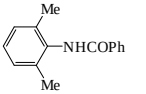
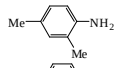
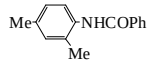
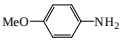
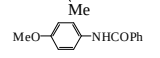
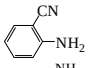
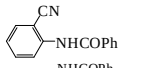
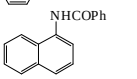
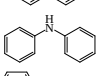
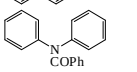
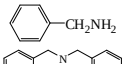
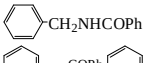
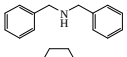
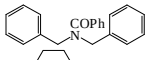
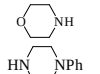
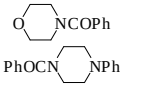
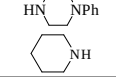
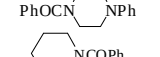
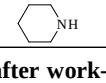
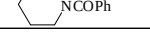
RESULTS AND DISCUSSION

The *N*-benzoylation reactions of amines by benzoyl chloride were investigated under solvent- and catalyst-free conditions using ultrasound irradiation at room temperature. As the reaction proceeds, the product precipitates as white crystals and separates at the end of the reaction. Benzoyl chloride is a very useful and eûcient reagent for production of peroxides, esters, amides, dyes, perfumes, pharmaceuticals and resins. It has been used as an acylating agent in acylation of functional groups. In most *N*-benzoylation procedures in the literature, excess of benzoyl chloride is used which cannot be easily recovered from the reaction mixture. The first principle of green chemistry states that it is better to prevent waste production than to treat waste or clean it up after it has been created[12]. In our methods, amides were prepared by application of stoichiometric amounts of benzoyl chloride (1.0 mmol) and amine (1.0 mmol) under solvent- and catalyst-free conditions. Waste production can be prevented when reagents are stoichiometrically treated. So, after completion of the reaction, there is no benzoyl chloride in the reaction mixture.

Also; no organic or aqueous solvents were used in the work-up step and the method did not require any purification steps such as column chromatography or recrystallization. Compared to the reported methods, our method is convenient, fast, safe and easy work-up.

To expand the scope of the current green protocol, a series of *N*-benzoylation reactions were carried out between various substituted aromatic, heterocyclic and aliphatic amines and benzoyl chloride at solvent- and catalyst-free conditions under ultrasound irradiation at room temperature (TABLE 1). In all cases, the results

TABLE 1 : Green *N*-benzoylation of different amines by the ultrasound irradiation

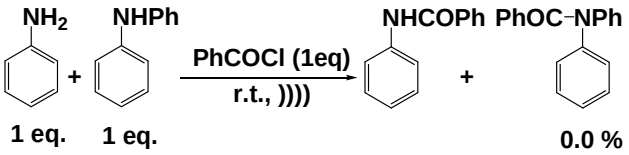
Entry	Substrate	Product	Time (min)	Yield[a] (%)
1			4	98
2			5	97
3			30	80
4			25	97
5			7	96
6			20	96
7			5	95
8			5	96
9			3	95
10			15	94
11			5	94
12			30	94
13			7	96
14			10	95
15			2	97
16			12	97
17			3	95

[a] **Yields are after work-up**

show that the reaction times are reduced and the yields are increased under sonication condition.

Anilines contain both electron-releasing and electron-withdrawing groups underwent the conversion in good yields (TABLE 1, entries 1-12). It was also found that the nature of the substitution on the aromatic ring of the aniline had no great influence on the reaction and all the substrates react with equal rates. In addition, naphthylamine (TABLE 1, entry 11) and benzylamine (Table 1, entry 13) were acylated to their *N*-benzoylated compounds in good yields. Interestingly, this method is applicable for the *N*-benzoylation of steric hindered amines such as diphenyl- and dibenzylamine as well (TABLE 1, entries 12 and 14).

The *N*-benzoylation of secondary amines need longer reaction times than primary ones; thus when a mixture of primary and secondary amines were exposed to benzoyl chloride (ratio of amine to benzoyl chloride, 1:1), only primary amine was benzoylated which shows the excellent chemoselectivity (Scheme 2).



Scheme 2 : Chemoselective *N*-benzoylation of amines

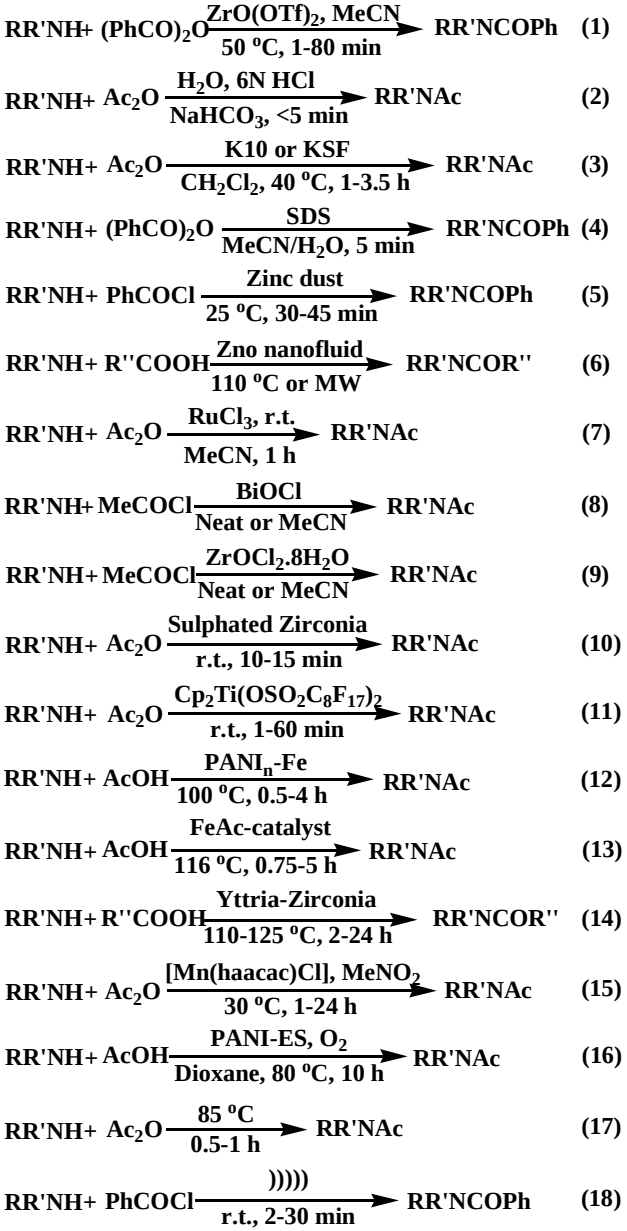
With those molecules containing both the hydroxyl and amino groups, only the *N*-benzoylated products were formed. So the *o*-benzoylation did not take place and the applied method shows a good chemoselectivity (TABLE 1, entries 4 and 5).

After a successful attempt with aromatic and aliphatic amines we further explored the reaction of benzoyl chloride with secondary heterocyclic amine such as morpholine (TABLE 1, entry 15), 1-phenylpiperazine (TABLE 1, entry 16) and pyrrolidine (TABLE 1, entry 17) which the reactions were successful as well.

Compared with the other literature works on the *N*-benzoylation of amines, the notable features of our method are:

- The reaction system is clean and simple;
- Organic solvents are not needed;
- Catalysts are not needed;
- Application of stoichiometric amounts of benzoyl chloride and amine;
- The yields are very high;
- High reaction temperatures and long reaction times are avoided;
- No side product was observed under the reaction conditions, thus this method did not require any further purification, and
- To the best of our knowledge, this new procedure provides the first example of an efficient ultrasound-promoted approach for the synthesis of amides.

Scheme 3 shows a nice comparison between the literature acylating methods (equations 1-17) with our proposed procedure (equation 18) to understand the



Scheme 3 : The *N*-benzoylation of amines under diffrent reaction conditions

advantages of the proposed method.

In most N-acylation procedures in the literature the following item are observed:

- Use of column chromatography or recrystallization for purification of the products;
- Use of toxic organic solvents in reaction mixture and in the extraction and purification steps;
- Use of acidic or basic reagents;
- Harsh reaction conditions (relatively high temperature, hazards,…..); and
- Use of homogeneous/heterogeneous reagent or catalysts.

All above items are wasting money and time consuming, so our proposed method can be considered as a green protocol which the reaction will take place in solvent- and catalyst-free conditions at room temperature.

The following disadvantages can be deduced from the literature about different amines *N*-acylations:

Disadvantages of equation (1)[18]

Application of volatile organic solvent (MeCN), use of excess $(PhCO)_2O$ as acylating agent which cannot be recovered at the end of reaction, use of catalyst, difficulties in preparation of the catalyst and availability of reagents, use of ether and aqueous solution of $NaHCO_3$ for extraction of the products and use of column chromatography for purification of the products. Also, this method is only limited to the acylation of primary amines.

Disadvantages of equation (2)[19]

Use of 6N HCl (hazardous, toxic, extremely corrosive and homogeneous reagent which decomposed during work-up and cannot easily be recovered and recycled) and use of sodium bicarbonate and ethyl acetate for extraction of the products. Also, this method is only limited to the acylation of primary amines.

Disadvantages of equation (3)[20]

Application of catalyst and volatile organic solvent (CH_2Cl_2), use of excess acetic anhydride as acylating agent which cannot be recovered at the end of reaction, long reaction times (1-3.5 h), harsh reaction conditions (reflux) and use of column chromatography for purification of the products.

Disadvantages of equation (4)[21]

Application of volatile organic solvent (MeCN), use of sodium dodecyl sulfate and use of sodium hydrogen carbonate and ethyl acetate for extraction of the products. This method is only limited to the acylation of primary amines.

Disadvantages of equation (5)[22]

Application of zinc dust as catalyst, use of excess benzoyl chloride as acylating agent which cannot be recovered at the end of reaction, use of ether, saturated $NaHCO_3$ solution and H_2O for extraction of the products and use of column chromatography for purification of the products. Also, this method is only limited to the acylation of primary amines.

Disadvantages of equation (6)[23]

Application of catalyst, difficulties in preparation of the catalyst and availability of reagents, harsh reaction conditions (110 °C or microwave irradiation, 475 W), use of excess carboxylic acid as acylating agent which cannot be recovered from the resulting reaction mixture and the use of ethyl acetate and aqueous solution of $NaHCO_3$ for extraction of the products. Also, this method is only limited to the acylation of primary amines and is not applicable for the *N*-acylation of secondary amines such as *N*-methylaniline or dipropylamine.

Disadvantages of equation (7)[24]

The use of $RuCl_3$ which cannot easily be recovered and reused, application of volatile organic solvent (MeCN), use of excess acetic anhydride as acylating agent which cannot be recovered from the resulting reaction mixture, use of ethyl acetate, saturated NH_4Cl solution, aqueous solution of $NaHCO_3$ and brine for extraction of the products and use of column chromatography for purification of the products.

Disadvantages of equation (8)[25]

Application of volatile organic solvent (MeCN) and $BiCl_3$, use of excess acetyl chloride as acylating agent which cannot be recovered from the resulting reaction mixture and use of CH_2Cl_2, brine, saturated $NaHCO_3$ solution for extraction of the products and the use of SiO_2 or recrystallization for purification of the products. Also, this method is only limited to the acylation of primary amines.

Disadvantages of equation (9)[26]

The use of $ZrOCl_2.8H_2O$ as catalyst which cannot

easily be recovered and reused, application of volatile organic solvent (MeCN), use of excess acetyl chloride as acylating agent which cannot be recovered from the resulting reaction mixture and use of CH_2Cl_2, brine, saturated $NaHCO_3$ solution for extraction of the products and the use of SiO_2 or recrystallization for purification of the products. Also, this method is only limited to the acylation of primary amines.

Disadvantages of equation (10)[27]

Application of sulphated zirconia as catalyst which cannot easily be recovered and reused, difficulties in preparation of the catalyst and availability of reagents and use of ethyl acetate and saturated bicarbonate solution for extraction of the products.

Disadvantages of equation (11)[28]

Application of catalyst, difficulties in preparation of the catalyst and availability of reagents, use of petroleum ether and brine for extraction of the products and use of column chromatography for purification of the products.

Disadvantages of equation (12)[29]

Application of catalyst, difficulties in preparation of the catalyst and availability of reagents, use of excess acetic acid as acylating agent and solvent which cannot be recovered from the resulting reaction mixture, high temperature requirement (100 °C), long reaction times (0.5-4 h) and use of column chromatography or recrystallization for purification of the products. Also, this method is only limited to the acylation of primary amines.

Disadvantages of equation (13)[30]

Application of catalyst, difficulties in preparation of the catalyst and availability of reagents, use of excess glacial acetic acid as acylating agent and solvent which cannot be recovered from the resulting reaction mixture, harsh reaction conditions (reflux), long reaction times (0.75-5 h) and use of ethyl acetate, saturated bicarbonate solution and brine for extraction of the products. Also, this method is only limited to the acylation of primary amines.

Disadvantages of equation (14)[31]

Application of catalyst, difficulties in preparation of the catalyst and availability of reagents, harsh reaction conditions (110-125 °C), use of excess carboxylic acid as acylating agent which cannot be recovered from the resulting reaction mixture, long reaction times (2-24 h), use of CH_2Cl_2, aqueous solution of $NaHCO_3$, brine and H_2O for extraction and use of column chromatography for purification of the products. Also, this method is only limited to the acylation of primary amines.

Disadvantages of equation (15)[32]

Application of organic solvent ($MeNO_2$), use of manganese(III) bis(2-hydroxyanil)acetylacetonato complex as catalyst which cannot easily be recovered and reused, difficulties in preparation of the catalyst and availability of reagents, use of excess acetic anhydride as acylating agent which cannot be recovered from the resulting reaction mixture and use of column chromatography for purification of the products.

Disadvantages of equation (16)[33]

Application of catalyst, difficulties in preparation of the catalyst and availability of reagents, application of organic solvent (dioxane), harsh reaction conditions (80 °C) and long reaction times (10 h).

Disadvantages of equation (17)[11,12]

Relatively high temperature (85 °C), use of excess acetic anhydride as acylating agent which cannot be recovered from the resulting reaction mixture, use of ether, aqueous sodium bicarbonate solution and brine for extraction of the products and use of distillation or column chromatography for purification of the products.

Advantages of equation (18)

None of the above mentioned disadvantages are observed. Also, application of ultrasound irradiation as an alternative energy source represents an interesting, fast and clean synthetic route. Reactions will take place at room temperature with high yields and easy operations without application of toxic organic solvents, bases, acids and expensive reagents or catalysts. This green procedure does not require any purification steps such as recrystallization and column chromatography since no by-product was formed.

CONCLUSIONS

In conclusion, a fast, economically and environmentally benign, highly efficient and safe procedure has been

developed for the *N*-benzoylation of amines under solvent- and catalyst-free conditions using ultrasound irradiation at room temperature. The current environmentally benign method is a green protocol since: (i) solvent (organic or aqueous), catalyst, heat (energy) and purification steps such as column chromatography or crystallization are not necessary to get the pure compounds; (ii) having excellent yields and reaction rates and simple methodology; (iii) cleaner reaction profiles; (iv) chemoselectivity and (v) easy work-up without any side products. The methodology can also be used for the introduction of other amine protecting groups.

This work was originally carried out to simplify the *N*-benzoylation process by omitting any solvent, catalyst and base, easier work-up, milder, cleaner and greener reaction, shorter reaction time, higher purity and yields, lower cost, and reducing the amount of waste or pollution which is very important from the economic, environmental and industrial points of view. This method proceeds with simple sonication of stoichiometric amounts of the amine and benzoyl chloride to provide the pure products in high yields.

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REFERENCES

[1] J.Otera; Esterification, Methods, Reactions and Applications, Wiley: Weinheim, **(2003)**.
[2] T.W.Greene, P.G.M.Wuts; Protecting Groups in Organic Synthesis, Third Edition, Wiley, New York, **(1999)**.
[3] G.Sartori, R.Maggi; Chem.Rev., **110**, PR1 **(2010)**.
[4] V.Theodorou, M.Gogou, M.Philippidou, V.Ragoussis, G.Paraskevopoulos, K.Skobridis; Tetrahedron, **67**, 5630 **(2011)**.
[5] M.Sathishkumar, P.Shanmugavelan, S.Nagarajan, M.Maheswari, M.Dinesh, A.Ponnuswamy; Tetrahedron Lett., **52**, 2830 **(2011)**.
[6] S.P.Chavan, R.Anand, K.Pasupathy, B.S.Rao; Green Chem., **3**, 320 **(2001)**.
[7] A.Orita, C.Tanahashi, A.Kakuda, J.Otera; Angew.Chem.Int.Edit., **39**, 2877 **(2000)**.
[8] E.Vedejs, S.T.Diver; J.Am.Chem.Soc., **115**, 3358 **(1993)**.
[9] E.Vedejs, O.Daugulis; J.Org.Chem., **61**, 5702 **(1996)**.
[10] B.C.Ranu, S.S.Dey, A.Hajra; Green Chem., **5**, 44 **(2003)**.
[11] K.Tanaka; Solvent-free Organic Synthesis, Wiley-VCH: Weinheim, **(2003)**.
[12] P.T.Anastas, J.C.Warner; Green Chemistry: Theory and Practice, Oxford University Press, New York, **(1998)**.
[13] T.J.Mason, D.Peters; Practical Sonochemistry, Second Edition, Ellis Horwood, London, **(2002)**.
[14] S.Koda, T.Kimurab, T.Kondoc, H.Mitomed; Ultrason.Sonochem., **10**, 149 **(2003)**.
[15] D.Habibi, M.Nasrollahzadeh, T.A.Kamali; Green Chem., **13**, 3499 **(2011)**.
[16] D.Habibi, M.Nasrollahzadeh; Monatsh Chem., **143**, 925 **(2012)**.
[17] D.Habibi, M.Nasrollahzadeh, A.Faraji, Y.Bayat; Tetrahedron., **66**, 3866 **(2010)**.
[18] M.Moghaddam, S.Tangestaninejad, V.Mirkhani, I.Mohammadpoor-Baltork, M.Babaghanbari, M.Zarea, L.Shariati, S.A.Taghavi; J.Iran.Chem. Soc., **6**, 523 **(2009)**.
[19] S.Naik, G.Bhattacharjya, V.R.Kavala, B.K.Patel; Arkivoc, **1**, 55 **(2004)**.
[20] T.S.Li, A.X.Li; J.Chem.Soc.Perkin Trans., **1**, 1913 **(1998)**.
[21] S.Naik, G.Bhattacharjya, B.Talukdar, B.K.Patel; Eur.J.Org.Chem., 1254 **(2004)**.
[22] M.A.Pasha, M.B.M.Reddy, K.Manjula; Eur.J. Chem., **1**, 385 **(2010)**.
[23] F.Tamaddon, F.Aboee, A.Nasiri; Catal.Commun., **16**, 194 **(2011)**.
[24] S.K.Di; Tetrahedron Lett., **45**, 2919 **(2004)**.
[25] R.Ghosh, M.Maiti, A.Chakraborty; Tetrahedron Lett., **45**, 6775 **(2004)**.
[26] R.Ghosh, M.Maiti, A.Chakraborty; Tetrahedron Lett., **46**, 147 **(2005)**.
[27] K.J.Ratnam, R.S.Reddy, N.S.Sekhar, M.L.Kantam, F.Figueras; J.Mol.Catal.A.Chem., **276**, 230 **(2007)**.
[28] R.Qiu, G.Zhang, X.Ren, X.Xu, R.Yang, S.Luo, S.Yin; J.Organomet.Chem., **695**, 1182 **(2010)**.
[29] P.R.Likhar, R.Arundhathi, S.Ghosh, M.L.Kantam; J.Mol.Catal.A.Chem., **302**, 142 **(2009)**.
[30] B.Sreedhar, V.Bhaskar, Ch.Sridhar, T.Srinivas, L.Kótai, K.Szentmihályi; J.Mol.Catal.A.Chem., **191**, 141 **(2003)**.
[31] P.Kumar, R.K.Pandey, M.S.Bodas, S.P.Dagade, M.K.Dongare, A.V.Ramaswamy; J.Mol.Catal. A.Chem., **181**, 207 **(2002)**.
[32] M.Salavati-Niasari, S.Hydarzadeh, A.Amiri, S.Salavati; J.Mol.Catal.A.Chem., **231**, 191 **(2005)**.
[33] C.W.Lee, H.Y.Hwang, H.M.Jeong, U.C.Yoon, K.W.Chi; Synthetic Met., **159**, 1820 **(2009)**.