ORIENTAL JOURNAL OF CHEMISTRY
An International Open Access, Peer Reviewed Research Journal
www.orientjchem.org
ISSN: 0970-020 X
CODEN: OJCHEG
2024, Vol. 40, No.(4):
Pg. 981-986

Investigation of New Procedure for Selective Reaction and Synthesis of Some New 2-Substituted Benzimidazole Derivatives

ARJUN BODKHE[1], DATTATRAYA PANSARE[2]*, DNYANESHWAR KARPE[1], VILAS SUDRIK[1], MANOHAR SURYAWANSHI[1] and SHAMRAO LAWANDE[1]*

[1]Department of Chemistry, Shri Chhatrapati Shivaji Mahavidyalaya, Shrigonda, 413701, Maharashtra, India.
[2]Department of Chemistry, Deogiri College Chhatrapati Sambhajinagar, 431005, Maharashtra, India.
*Corresponding author E-mail: splawande@gmail.com, dattatraya.pansare7@gmail.com

http://dx.doi.org/10.13005/ojc/400408

(Received: June 12, 2024; Accepted: August 21, 2024)

ABSTRACT

The objective of this study is to investigate a new procedure for specifically reducing the NO_2 group present on the aromatic ring along with ester group. We revealed that $NaBH_4$-$FeCl_2$ serves as a crucial reagent in this process. The reduction mediated by $NaBH_4$-$FeCl_2$ exhibited remarkable chemoselectivity, yielding the wanted products in outstanding yields of up to 90-95%. Furthermore, this process was successfully utilized in the synthesis of diamino compound, and in the synthesis of 2-substituted benzimidazole derivatives The diamine compounds was condensed with various aromatic or heterocyclic carboxylic acids in the existence of EDC.HCl and catalyst DMAP. The resulting moiety or product underwent cyclization by using CH_3COOH at 100-110°C. Both the reactions (coupling & cyclization) reaction completed effectively, within the minimal reaction times. The structure of created compounds was confirmed using modern spectral techniques like FT-IR, mass spectrometry, NMR.

Keywords: $NaBH_4$-$FeCl_2$, Benzimidazole, EDC.HCl, DMAP, Green synthesis.

INTRODUCTION

The Benzimidazole pharmacophore stands as a pipathogensrocyclic element within a plethora of pharmaceutical[1,2]. Because of their broad spectrum of bioactivity, this compounds class has captured the interest of medicinal and organic chemists, spurring the exploration of diverse synthetic methodologies.[3] With seven positions available for substitution, the benzimidazole moiety offers a canvas for the manifestation of unique and varied bioactivities across various drug classes[4]. Notably, compounds featuring the benzimidazole pharmacophore find utility in numerous therapeutic areas, including antimicrobial[5] and antiviral agent combating pathogens[6-14].

The remarkable diversity in bioactivity spurred chemists to explore various synthetic routes for benzimidazole synthesis. Initially, benzimidazoles were readily obtained through the condensation of diamine with compound containing functional groups like -COOH, -CN, and $RC(OR')_3$[15]. Though, this method is disadvantaged by drawbacks such as lesser yields, the formation of impurities[16] . Moreover, employing catalysts like Titanium containing catalyst, cumene hydroxide[17], has confirmed to offer good to better yields.

Additionally, metal Ru,[18] Pd[19] and Rh[20] catalysts also employed in the creation of benzimidazole. However, described approaches for producing 2-substituted benzimidazole moiety often lack compatibility with diverse functional group or several starting materials revealing varying substitution designs. Furthermore, they typically necessitate high-priced catalysts, elevated temperature, or harsher reaction circumstances, like the use of hazardous acid for reactions. Accordingly, these approaches may not be conductive to kilo-scale production.

The objective of this research was to investigate a new method for selectively reducing the NO_2 group without affecting the RCOOR'group. In this finding, $NaBH_4$-$FeCl_2$ was identified as a crucial reducing agent in the process, resulting in the formation of the corresponding amino compound. The reduction mediated by $NaBH_4$-$FeCl_2$-demonstrated high chemo selectivity, yielding the desired products in impressive yields (up to 90-95%). Furthermore, this method was utilized to synthesis of dabigatran intermediate. (anticoagulant drug) and the synthesized di-amino compound. This was reacted with various Carboxylic acids by using coupling reagent like EDC.HCl and cat. DMAP, and subsequently cyclized by using CH_3COOH at reflux to yield 2-substituted benzimidazole derivatives.

RESULT AND DISCUSSION

The investigation into reduction condition was carried out as detailed illustrated Table 1. Our finding commenced using substrate 3. Firstly, the reaction was performed with 1.0 equit. of MXn and 2.5 equit. of $NaBH_4$ under an inert environment in THF at 25-30 °C. The exhibited process was sluggish, resulting in only a 12% yield to the desired product **3** when $CuSO_4$ was utilized (Entry i in Table 1) and when using $AlCl_3$ or LiCl, yielding 35.5% and 5% respectively (Entries ii,iii in Table 1). Interestingly, we have observed that when used metal salts good to moderate yield was obtained. Subsequently, various ferrous salts were assessed, revealing $FeCl_2$ as optimal, achieving high yield (up to 93.2%), whereas other salts give less yield (< 35%, Entries v,vii,viii in Table 1). Tried to reduce the amount of $NaBH_4$ led to significant decreases in yield when reducing the loading from 2.5 equit. to 1.5 or 1.1 equit. (Entries vi and ix-xi in Table 1). Furthermore, experimentation with different quantities of $FeCl_2$ indicated that 1.0 equiv.was optimal, with decreasing equivalents resulting in less yield. (Entries xii-xiv in Table 1). Solvent choice significantly influenced the reaction, with aprotic solvents favoring high yield, while in polar Solvent yielded poor results (Entry vi, xv, xvi in Table 1). Consequently, Tetrahydrofuran was preferred as a solvent. Lastly, impact of reaction temperature on assessed, revealing decreased yield (Entry xvii in Table 1). Attempts to enhance the rate by elevating temperature to 40-45°C yielded unexpectedly low yield (Entry xviii in Table1). Ultimately, the optimal reaction conditions were established as 2.5 equit. of $NaBH_4$, 1.0 equit. of $FeCl_2$, THF, and a reaction temp. of 25-30°C.

Table 1: Optimization of Reagent, its equivalent, solvent selection and reaction temperature

Entry	MXn(eq.)	NaBH4 (eq.)	Solvent	Output (%)	Temperature (°C)
1	$CuSO_4$ (1.0)	2.5	THF	12.0	25-30°C
2	$AlCl_3$(1.0)	2.5	THF	35.5	25-30°C
3	LiCl(1.0)	2.5	THF	5.3	25-30°C
4	$FeCl_3.6H_2O$(1.0)	2.5	THF	3.7	25-30°C
5	$FeCl_3.7H_2O$(1.0)	2.5	THF	25.3	25-30°C
6	$FeCl_2$(1.0)	2.5	THF	93.2	25-30°C
7	$FeBr_2$(1.0)	2.5	THF	3.8	25-30°C
8	$FeC_2O_4.2H_2O$(1.0)	2.5	THF	12.8	25-30°C
9	$FeCl_2$(1.0)	2.0	THF	83.20	25-30°C
10	$FeCl_2$(1.0)	1.5	THF	61.2	25-30°C
11	$FeCl_2$(1.0)	1.1	THF	18.3	25-30°C
12	$FeCl_2$(0.8)	2.5	THF	85.0	25-30°C
13	$FeCl_2$(0.5)	2.5	THF	72.0	25-30°C
14	$FeCl_2$(0.2)	2.5	THF	36.0	25-30°C
15	$FeCl_2$(1.0)	2.5	MeCN	78.0	25-30°C
16	$FeCl_2$(1.0)	2.5	EtOH	17.5	25-30°C
17	$FeCl_2$(1.0)	2.5	THF	23.6	10-15°C
18	$FeCl_2$(1.0)	2.5	THF	34.6	40-45°C

Benzimidazole derivatives prepared through the reaction of di amino compound with several aromatic compounds that have COOH gr., Catalyzed by EDC.HCl and cat. DMAP. The resulting coupled compounds were then cyclized in CH_3COOH at 100-110°C (Scheme 1). The reaction supervised by TLC.

We selected the reaction between synthesized di-amino compound and Benzoic acid as a model reaction for optimization of coupling reagent and reagent which increase the rate of reaction. Initially, we conducted the model reaction using Thionyl Chloride & TEA, which resulted in lower conversion and isolated yield. Subsequently, we explored different coupling reagents like DCC-HOBt Carbonyldimidazole, EDC.HCl-DMAP (Entries ii-iv in Table 2). We have found that DCC-HOBt and Carbonyldimidazole (Entries II-III in Table 2) yielded only 83% and 80% respectively. The optimal result, boasting a 90% yield for product 3a, was attained through the utilization of coupling reagent EDC.HCl /DMAP (Entries iv in Table 2).

Table 2: Optimization of Coupling reagent along with reaction time and outcome

Entry	Reagent	Time (Minutes)	Output(%)[a]
1	$SOCl_2$ & TEA	60	75
2	DCC-HOBt	60	83
3	Carbonyldimidazole	60	80
4	EDC.HCl-DMAP	60	90

[a]Isolated yield

Various reagents, including (HBTU) and (TBTU), Hydroxybenzotrizole (HOBt), 4-Dimethylaminopyridine (DMAP) were also investigated to accelerate reaction rate of reaction with coupling reagent. Applying the similar 6a reaction as an example, we initially conducted the reaction as such without any reagents (Entry i in Table 3), which necessitated a prolonged reaction time of approximately 360 to 420 minutes. However, the inclusion of catalytic amounts of HOBt, HBTU, TBTU, and DMAP (Entries ii-v in Table 3) significantly expedited the reaction, reducing the reaction time to just half an hour. While both reagents proved effective, we opted for DMAP due to safety considerations in enhancing the reaction rate.

Table 3: Optimization of Catalyst

Entry	Catalyst	Time (min)	Output(%)[a]
1	--	360	80
2	HOBt	60	83
3	HBTU	90	80
4	TBTU	90	81
5	DMAP	60	90

[a]Isolated yield

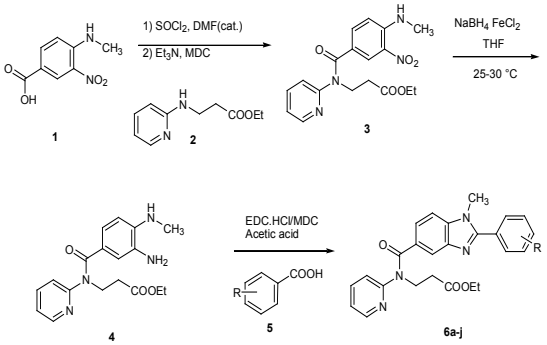
Different acids, including 4N HCl, Acetic acid, Formic acid, Ammonium chloride, polyphosphoric acid and ortho phosphoric acid were also investigated in cyclization reaction. we initially conducted reaction with 4N HCl, but we got less yield. Next, acid (Entries ii-v in Table 4). It was found that only 73%, 78%,76%, and 75% yield was obtained by using Formic acid, NH_4Cl, Polyphosphoric acid, Ortho-phosphoric acid respectively. CH_3COOH facilitates cyclization efficiently, providing good yields in a shorter reaction time. (Entry vi in Table 4).

Table 4: Optimization of Acid, reaction time and output for cyclization

Entry	Acid reagent	Time (min)	Output(%)[a]
1	4NHCl	120	74
2	Formic acid	100	73
3	NH_4Cl	120	78
4	Polyphosphoric acid	100	76
5	Ortho-phosphoric acid	100	75
6	Acetic Acid	60	90

[a]Isolated yield

By employing these optimized reaction conditions, a range of benzimidazole derivatives 4a-j were efficiently produced within a quicker timeframe and with enhanced yields. This synthesis utilized EDC.HCl and DMAP as coupling reagents, along with a CH_3COOH acid assisting in the cyclization.



Scheme 1. Synthesis of Some New Benzimidazole derivatives (6a-j)

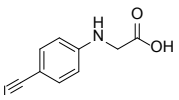
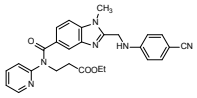
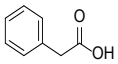
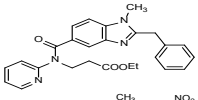
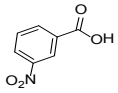
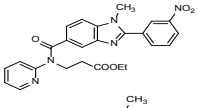
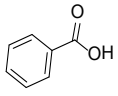
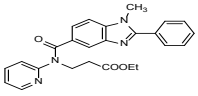
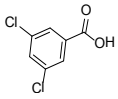
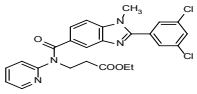
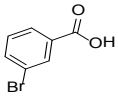
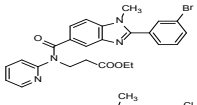
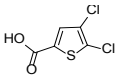
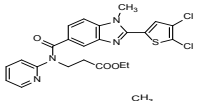
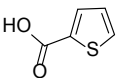
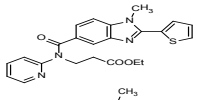
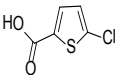
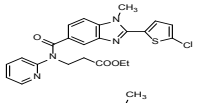
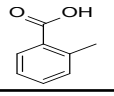
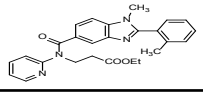
This approach utilized to produce a series of new Benzimidazole (2-substituted) derivatives. The outcomes succinctly presented in Table 5.

Our current procedure was applied to a diverse array of several carboxylic acids to demonstrate its broad utility, as outlined in Table 3. It was observed that both unsubstituted and electron-withdrawing substituent-bearing aromatic and heteroaryl carboxylic acids underwent smooth conversion, yielding products and purified by using Flash chromatography solvent (Table 3). Compounds (**6a, 6d,** and **6f**) lacking substituents, as well as some compounds with electron-withdrawing substituents (**6b, 6c, 6e, 6h, 6i** and **6j**) such as (CN) Cyano, (Br) Bromo, (Cl) Chloro, dichloro, and NO_2(Nitro) respectively, were synthesized successfully. Nevertheless , in the preparation of compounds **6a-6j,** it was detected that when substituents presented on ortho position, several carboxylic acids resulted in impure compounds, requiring purification through flash chromatography, resulting in a lower yield for compounds **6g**. Additionally, attempts were made to synthesize benzimidazole derivatives using aromatic acid which ortho substituted aromatic benzoic acid. However, these substituted acids exhibited lower reaction conversion rates.

Spectral data for the representative compound (6a)

The FT-IR spectrum shows a peak at 1723 cm^{-1} confirming the presence of a carbonyl group, and a peak at 3397 cm^{-1}, indicating NH groups in the structure. The ^1H NMR spectrum shows a chemical shift between 7.50–7.13, suggesting the presence of aromatic protons. The chemical shift at 3.75 (s, 3H) confirms that a methyl group is attached to the nitrogen atom in the structure. The molecular weight of the compound is 483.213 $[M+1]^+$, which exactly matches the reported structure.

Table 5: Synthesis of 2-Substituted benzimidazole (6a-j)

Sr. No	Carboxylic acid	Compound	Yield (%)	m.p. °C
6a			85	117-119
6b			89	126-128
6c			88	148-149
6d			90	108-110
6e			84	188-190
6f			86	128-130
6g			84	119-121
6h			85	88-90
6i			86	98-100
6j			45	121-123

EXPERIMENTAL

MATERIAL AND METHODS

Compounds were sourced from a commercial vendor, while reagents and analytical grade (A.R.) solvents were procured from Sigma-Aldrich. The reaction progress was monitored via Thin Layer Chromatography (TLC) on silica plates (Merck silica gel 60F254). Column chromatography was carried out using silica gel with a 60–120 mesh size.

Instrumentation

The FT-IR Spectra recorded at 100 FT-IR; Mass spectra recorded at Advion Expression CMS instrument. The PMR spectra were recorded on 400MHz, and CMR spectra recorded on 100MHz Brucker spectrometer in DMSO/$CDCl_3$ using Brucker instrument. The chemical shift value was recorded with respect to standard Tetramethylsilane.

Reaction conditions

The glassware utilized for reactions underwent thorough washing and cleaning procedures before being dried at 150°C and subsequently cooled under vacuum conditions.

Experimental procedure

General method for the preparation of compound (3)

Compound 1 (5.09 mmol) dissolve in CH_2Cl_2 (5 mL) and Cat. amount DMF, cool it to 0-10°C then add dropwise $SOCl_2$ (7.63 mmol)in 10 minute. Raise the temperature to 20-30°C and stirred for 60 min at 20-30°C, monitoring reaction TLC. After completion of reaction, concentrate reaction mixture and degassed for 30 minutes. Obtained residue cooled to 20-30°, added CH_2Cl_2 (5 mL), triethyl amine(10.18mmol) and stirred for 10 minute. Cool it at 0-5° then added dropwise solution of Compound 2 (4.581mmol) in CH_2Cl_2 (5 mL), raised temperature to 20-30°C and stirred for 30 minutes. monitor reaction by TLC.After completion of reaction added a $NaHCO_3$ (5 mL) solution to reaction mix. and separate the organic layer and wash with water(5 mL). Concentrate under vacuum and obtain crude residue crystallized form hexane to get pure Compound 3. (1.30 g, 79.3%) as Pale Yellow solid.

General method for the preparation of compound (4)

Compound 3 dissolved in THF (10 mL) and stirred for 10-15 min, add $FeCl_2$ (3.22 mmol) followed by $NaBH_4$ (8.05 mmol) under argon/ Nitrogen atmosphere and stir for 720 min at 20-30°C, monitoring reaction on TLC. After complete consumption of compound 3, water (20 mL) was added, Organic extract extract with Ethyl Acetate. wash with water. Concentrate the organic layer to form Crude residue and column chromatography used to get the pure compound 4 (1.01 g, 93.2%).

The General method for the preparation of compound (6a-j)

To a stirred mixture of the compound 4 (1.46mmol) and DMAP(0.146mmol) in CH_2Cl_2 (10mL) added the different carboxylic acid (1.75mmol) in CH_2Cl_2 (5 mL) in one portion at RT. The resulting blend stir at 20-30°C for 60 minutes. Afterward reaction monitored by TLC.After completion of reaction added water (10 mL). Separate the organic layer Organic layer and then organic layer successively wash with $NaHCO_3$ solution and water. The organic layer dried over Na_2SO_4. Concentrated under vacuum, obtained oily residue degassed for 30 minute. Obtained residue cool to 20-30°C, add Acetic acid (5 mL), stirred for 5-10 minute. Raised temperature 100-110°C and stirred for 60 minute. Cool reaction mix to 20-30°C, added water (25 mL) and extracted with CH_2Cl_2. The organics wash with 5% $NaHCO_3$ solution, dried by using Na_2SO_4 and concentrate. The resulting residue purified by using flash chromatography technique to provide the product **6a-j**. (0.56g, 90%).

Spectral data

Compound (3): Pale Yellow solid, Yield: 79.3%, m.p. 88-90°C, FT-IR (cm^{-1}): 3382, 1721, 1648,1620, 1566, 1368, 1270, 1175. ^{1}HNMR ($CDCl_3$, δppm): δ 8.47 (d, 1H), 8.14 (br, 2H), 7.53 (t, 1H), 7.43 (d, 1H), 7.11 (dd, 1H), 6.87 (d, 1H), 6.66 (d, 1H), 4.37 (t, 2H), 4.09 (t, 2H), 2.98 (d, 3H), 2.79 (t, 2H), 1.23 (t, 3H). ^{13}CNMR ($CDCl_3$, δ ppm): δ 171.68, 168.44, 156.08, 149.24, 147.00, 137.79, 136.35, 130.80, 128.70, 122.25, 122.17, 121.50, 112.78, 60.57, 44.97, 33.22, 29.78, 14.14. ESI-MS m/z: 373.150 $[M+1]^+$.

Compound (4): Light yellow, Yield: 94.9 %, m.p. 141-143°C. FT-IR (cm^{-1}): 3359,2986, 1729,1634 (1592,1569,1378, 1191,1154. ^{1}H NMR (DMSO-d_6, δ ppm): δ 8.41 (m,1H), 7.57 (dt, 1H), 7.20 (m, 1H), 6.78 (d, 1H), 6.67 (d, 1H), 6.34 (dd, 1H), 6.11 (d, 1H), 5.10 (br, 1H), 4.55 (br, 2H,), 4.18 (t, 2H), 3.97 (q, 2H), 2.65 (s, 3H), 2.65 (t, 2H), 1.12 (t, 3H). ^{13}C NMR (DMSO-d_6, δ ppm): δ 171.56, 171.10, 157.00, 148.84, 139.88, 137.82, 135.52, 123.18, 122.24,

120.93, 120.36, 115.59, 107.33, 60.41, 44.47, 33.63, 30.18, 14.44. ESI-MS m/z : 341.162[M+1]$^+$.

Compound (6a): Pale yellow, Yield: 85%, m.p.: 117-119°C. FT-IR (cm^{-1}): 3397, 2979, 1723, 1630, 1605, 1584, 1378, 1179, 1127. ^{1}HNMR (DMSO-d_6, δ ppm): δ 8.40 (d, 1H),7.50 (m, 3H), 7.39 (d, 1H), 7.28 (br, 1H), 7.19 (d, 1H), 7.13 (t, 2H), 6.88 (m, 3H), 4.60 (d, 2H), 4.24 (t, 2H), 3.97 (q, 2H), 3.75 (s, 3H), 2.71 (t, 2H), 1.13 (t, 3H). ^{13}CNMR (DMSO-d_6, δ ppm): δ 172.52, 171.79, 156.48, 153.79, 152.22, 149.16, 141.27, 138.34, 137.70, 133.79, 129.82, 123.33, 122.58, 121.71, 120.91, 120.01, 112.84, 109.97, 97.5, 60.49, 44.84, 40.12, 33.50, 30.35, 14.42. ESI-MS m/z: 483.213 [M+1]$^+$.

CONCLUSION

In conclusion of our research work, $NaBH_4$-$FeCl_2$ was revealed as a major reductant in the process resulting in the formation of the corresponding amino compound. $NaBH_4$-$FeCl_2$-mediated reduction proven high chemo selectivity, gave the required products in impressive yield (up to 90-95%). The synthesized di-amino compound condensed with several carboxylic acids (aromatic) in the existence of EDC.HCl and cat. DMAP, and insitu cyclization by using Acetic acid. The conditions are gentle, allowing for the tolerance of wide range of functional groups. This condensation reaction offers several advantages: it can be carried out using affordable, readily available chemicals, under extremely simple reaction conditions, with short reaction times, extraordinary yields. Additionally, it employs simple experimental techniques, is cost-economical, and associates with the bases of green chemistry. The biological activity of synthesized compounds will take in due course and hope it will be shows better activity against tested strains.

ACKNOWLEDGMENT

The authors thankful to The Principal, Shri Chhatrapati Shivaji Mahavidyalaya, Shrigonda, 413701, Maharashtra, India for providing the laboratory facility.

Conflicts of interest

The authors (s) declare(s) that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. Bhattacharya, S.; Chaudhuri, P., *Curr. Med. Chem.*, **2008**, *15*(18), 1762-1777.
2. Horton, D. A.; Bourne, G. T.; Smythe, M. L., *Chem. Reviews.*, **2003**, *103*, 893-930.
3. Pozharskii, A. F.; Garnovskii, A.; Simonov, A. M., *Minnesota Mining and Manuf.*, **1966**, *35*, 386.
4. Velík, J.; Baliharová, V.; Fink-Gremmels, J.; Bull, S.; Lamka, J.; Skálová, L., *Res. Veterinary Sci.*, **2004**, *76*, 95-108.
5. Fonseca, T.; Arbara Gigante, B.; Gilchrist, T.L., *Tetraheron.*, **2001**, *57*, 1793-1799.
6. Roth, T.; Morningstar, M. L.; Boyer, P.L.; Hughes, S. H.; Buckheit, R.W.; Michejda, C. J., *J. Med. Chem.,* **1997**, *40*, 4199-4207.
7. Migawa, M.T.; Girardet, J.L.; Walker 2nd, J. A., Koszalka, G. W.; Chamberlain, S. D.; Drach, J. C.; Townsend, L. B., *J. Med. Chem.*, **1998**, *41*, 1242-1251.
8. Denny, W.; Rewcastle, G.; Baguley, B., *J. Med. Chem.*, **1990**, *33*, 814-819.
9. Sondhi, S.M.; Singh, N.; Kumar, A.; Lozach, O.; Meijer, L., *Bioorg. Med. Chem.*, **2006**, *14*, 3758-3765.
10. Yang, D.; Fokas, D.; Li, J.; Yu, L.; Baldino, C. M., *Synthesis.*, **2005**, *1*, 47-56.
11. Valdez, P. D.; Rodríguez, M. S.; Hernández, C. A.; Lilián, Y. M.; Tapia, C. A.; Castillo, R., *Bioorg. Med. Chem.*, **2009**, *17*, 1724-1730.
12. Anisimova, V.; Avdyunina, N.; Spasov, A., *Pharm. Chem. Journal.*, **2002**, *36*, 377-381.
13. Bai, Y.; Lu, J.; Shi, Z.; Yang, B., *Synlett.*, **2001**, *4*, 544-546.
14. Hasegawa, E.; Yoneoka, A.; Suzuki, K.; Kato, T.; Kitazume, T.; Yanagi, K., *Tetrahedron.*, **1999**, *55*, 12957-12968.
15. Dudd, L.; Venardou, E.; Garcia, V.; Licence, P.; Blake, A.; Wilson, C.; Poliakoff, M., *Green Chemistry.*, **2003**, *5*, 187-192.
16. Nagata, K., ITIH & OA., *Heterocycles.*, **2003**, *61*, 105.
17. Havaldar, F.; Mule, G.; Dabholkar, B., *Syn. Comm.*, **2011,** *41*, 2304-2308.
18. Chakrabarty, M.; Karmarkar, S.; Mukherji, A.; Arima, S.; Harigaya, Y., *Heterocycles.*, **2006**, *68*, 967-974.
19. Aliyan, H.; Fazaeli, R.; Fazaeli, N.; Mssah, A.; Naghash, H. J.; Alizadeh, M.; Emami, G., *Heteroatom Chem.*, **2009**, *20*, 202-207.
20. Zhang, Z.; Yin, L.; Wang, Y., *Cat. Communications.*, **2007**, *8*, 1126-1131.