# An Unexpected Role of Carbon Disulfide: A New and Efficient Method for the Synthesis of 2-Substituted Benzimidazoles

by **John A. Gladysz**[*a]), **Hamid Reza Safaei**[*a])[b]), and **Sara Nouri**[b])

[a]) Department of Chemistry, Texas A&M University, P.O. Box 30012, College Station, Texas 77842-3012, USA (gladysz@chem.tamu.edu)

[b]) Department of Applied Chemistry, Faculty of Science, Shiraz Branch, Islamic Azad University, P.O. Box 71993-5, Shiraz, Iran (phone: +98-71-36402715; fax: +98-71-36412488; e-mail: hamid.safaei@chem.tamu.edu; safaei@iaushiraz.ac.ir)

Dedicated to Professor *A. Shaabani* for his great contribution to the development of Organic Chemistry in Iran

A new and efficient methodology for the synthesis of 2-substituted benzimidazoles is described. In this procedure, $CS_2$ unexpectedly facilitated the cyclization reaction between benzene-1,2-diamine and benzenecarbaldehydes in $CH_2Cl_2$ at room temperature. The reactions occur under mild conditions require simpler equipment and easier workup procedures.

**Introduction.** – In 1860, reported on red crystalline adducts that formed by the reaction between the newly discovered trialkylphosphines and carbon disulfide ($CS_2$) [1]. Hundred years later, their zwitterionic phosphoniodithioformate (dithiocarboxylatophosphonium) structures were established by X-ray crystallography [2] (*Fig*).

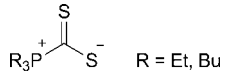
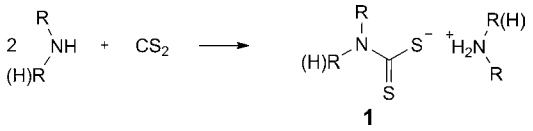



Figure. *Adduct of trialkylphosphine and $CS_2$*

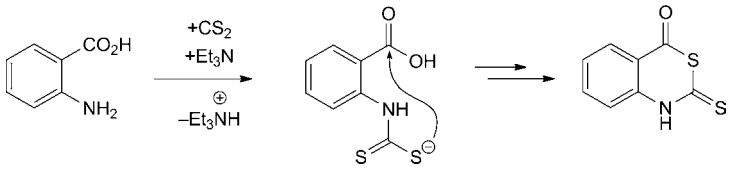
Although there are many reports on the reaction of nucleophiles and $CS_2$ [3], these adducts have been less investigated, and there are only a few reports about the reaction of these types of trialkylphosphine 1,3-dipoles in the literature [4]. In recent years, they attracted more attention because of their ability to produce organosulfur compounds [5]. Moreover, during the last decade increased attention has been focused on the development of the reaction between amines, $CS_2$, and electrophilic reagents [6]. Carbamodithioates **1** have been obtained from the nucleophilic reaction between amines and $CS_2$ (*Scheme 1*) [7]. Subsequently, attack to different electrophiles such as halides, epoxides, and $\alpha,\beta$-unsaturated carbonyl compounds led to dithiocarbamates.

Previously, *Saidi* and co-workers reported the reaction of oxiranes with $CS_2$ for the synthesis of cyclic dithiocarbonates, catalyzed by an organic base such as 4-(dimethylamino)pyridine or $Et_3N$, in good yields [8]. Recently, *Gütschow* and co-workers have investigated the reaction mechanism of anthranilic acid and $CS_2$ in the presence of catalytic amounts of $Et_3N$ at room temperature (*Scheme 2*) [9].

Scheme 1. *Reaction of Amines and $CS_2$*



Scheme 2. *Reaction of Anthranilic Acid and $CS_2$ Catalyzed by $Et_3N$*

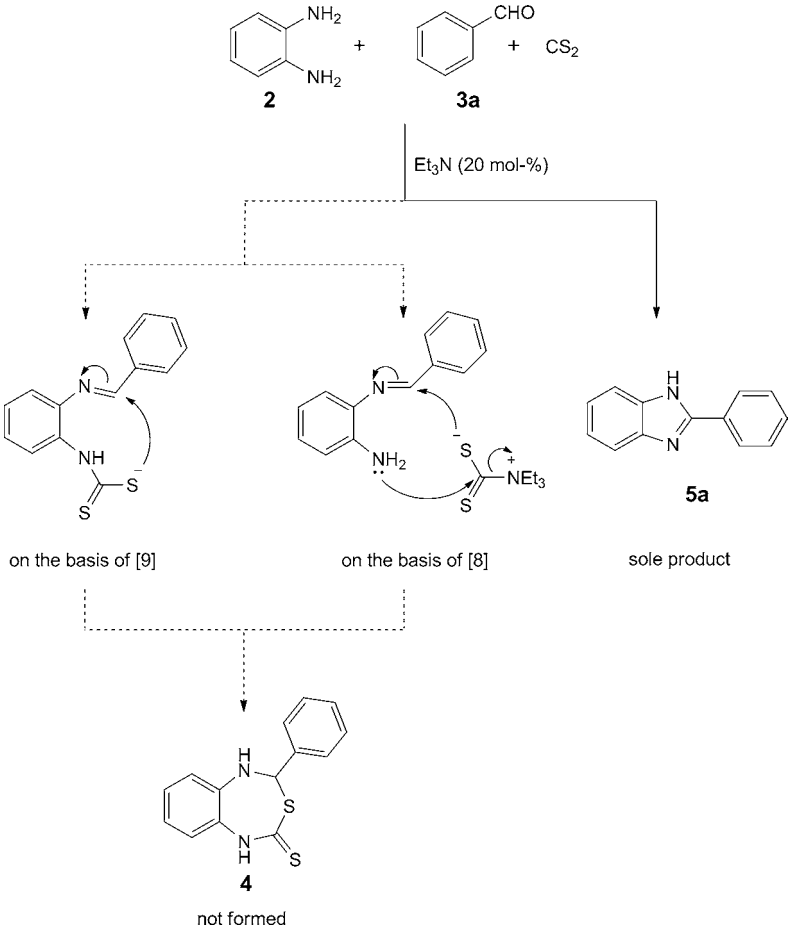


On the basis of the above reports, due to the importance of the biological activity of 1,4-benzothiazepines [10], and as part of our ongoing program to develop new and efficient methods for the synthesis of biologically active compounds from readily available building blocks [11], we conducted a study to achieve an efficient synthesis of seven-membered heterocycles of type **4** by the reaction of benzene-1,2-diamine, PhCHO, $CS_2$, and catalytic amounts of $Et_3N$ in $CH_2Cl_2$ at room temperature (*Scheme 3*).

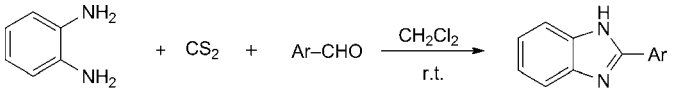
**Results and Discussion.** – Surprisingly, when **2** was reacted with 1 equiv. of **3a** and $CS_2$ in the presence of catalytic amounts of $Et_3N$ after extended reaction times up to 16 h, the desired product **4** was not obtained. Instead, a colorless product was isolated with a $^1$H-NMR resonance at $\delta$(H) 12.9 corresponding to a N–H moiety related to 2-phenyl-1*H*-benzimidazole (**5a**). A *singlet* signal at $\delta$(H) of *ca.* 5 expected for H–C(4) of compound **4** did not appear. The $^1$H-NMR spectrum of the product exhibited *multiplet*s at $\delta$(H) 7.2–8.2 corresponding to nine aromatic H-atoms. The $^{13}$C-NMR spectrum also showed eleven distinct signals at $\delta$(C) 109.9–150.6, fully supporting the structure **5a**. Moreover, the structure of the product was supported by elemental analysis and its IR spectrum. The melting point also confirmed the structure of **5a** as compared with an authentic sample [12]. For the evaluation of the role of the amine and $CS_2$ on the reaction product, the reaction was performed in the absence of $Et_3N$ and $CS_2$ separately. Unexpectedly, we found that in the absence of the amine, the benzimidazole **5a** was obtained as the sole product (*cf. Table 1*, *Entry 5*). However, the product was not obtained in the absence of $CS_2$ (*cf. Table 1*, *Entries 2* and *3*). Thus, a new and efficient method for the synthesis of 2-substituted benzimidazoles was developed (*Scheme 4*).

In this procedure, $CS_2$ unexpectedly facilitates the cyclization reaction between benzene-1,2-diamine and aromatic aldehydes at room temperature. The reactions occur under mild conditions and require simpler equipment and easier workup procedures. Moreover, unlike most other methods for this synthesis, the method does not require acid and metallic catalyst. Furthermore, it may allow access to some derivatives of benzimidazole derivatives that require harsh reaction conditions under traditional approaches.

Scheme 3. *Reaction of Benzene-1,2-diamine, PhCHO, and $CS_2$ in the Presence of $Et_3N$*




Scheme 4. *Synthesis of 2-Subsituated Benzimidazoles*




**2** **3a – 3o** **5a – 5o**

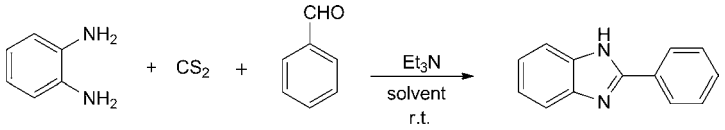
2-Substituted 1*H*-benzimidazoles are one of the most important classes of N-heterocycles that have recently been evaluated as DNA minor-groove binding agents with antitumor activity [13], and as ligands to transition metals for modelling biological systems [14]. They are widely used in medicinal chemistry because of their diverse biological features, such as fungicidal, antitumor, immunosuppressant, and anticonvulsant activities [15]. Based on these findings, the synthesis of 1*H*-benzimidazole derivatives is currently of great interest in organic synthesis [16]. The most frequently applied method for the synthesis of 2-substituted 1*H*-benzimidazoles are based on the

reaction of benzene-1,2-diamine with carboxylic acids or aldehydes catalyzed by strong acids and transition-metal salts such as $Sc(OTf)_3$, $Ru(PPh_3)_3(CO)H_2$, and ceric ammonium nitrate (CAN) [12][17].

Moreover, in recent years, unconventional reagents such as 1,2-dihalobenzene, *N*-(2-haloaryl)benzamidine, bis(1,2-haloaryl)carbodiimide, and 2-azidoaniline were used instead of benzene-1,2-diamine in the presence of Pd or Cu complexes as catalyst [18]. Most of these methods have certain limitations such as tedious processes, harsh reaction conditions, application of hazardous catalysts, generation of toxic metal reagents, and low yields of products. Additionally, in view of the pharmaceutical application of arylbenzimidazoles and due to potentially toxic contamination of pharmaceutical products, effective removal of some metals such as Pd or Cu in active pharmaceutical ingredients (API) provides important health benefits [19]. So, it has been worthwhile to search for practical metal-free conditions.

We first attempted to optimize the reaction conditions for the synthesis of 2-phenyl-1*H*-benzimidazole by the reaction between benzene-1,2-diamine (1 mmol) and PhCHO (1 mmol) in the presence of various amounts of $CS_2$ in $CH_2Cl_2$ at room temperature (*Table 1*).

Table 1. *Influence of Different Amounts of $CS_2$ and $Et_3N$ on the Reaction between Benzene-1,2-diamine and PhCHO Leading to 2-Phenyl-1*H*-benzimidazole* (**5a**), *in Different Solvents at Room Temperature*




**2** **3a** **5a**

| *Entry* | Solvent | $CS_2$ [mmol] | $Et_3N$ [mmol] | Time [h] | Yield [%][a]) |
|---|---|---|---|---|---|
| *1* | $CH_2Cl_2$ | 1 | 0.2 | 16 | 91 |
| *2* | $CH_2Cl_2$ | – | 0.2 | 24 | ng[b]) |
| *3* | $CH_2Cl_2$ | – | 1 | 24 | ng |
| *4*[c]) | $CH_2Cl_2$ | – | 1 | 24 + 16 | 89 |
| *5* | $CH_2Cl_2$ | 1 | – | 16 | 92 |
| *6*[d]) | $CH_2Cl_2$ | 2.5 | – | 7 | 37 |
| *7*[d]) | $CH_2Cl_2$ | 5 | – | 8 | 43 |
| *8*[d]) | $CH_2Cl_2$ | 10 | – | 8 | 41 |
| *9* | $CH_2Cl_2$ | 0.2 | – | 24 | 28 |
| *10* | $CH_2Cl_2$ | 0.5 | – | 24 | 42 |
| *11* | $CH_2Cl_2$ | 0.8 | – | 24 | 69 |
| *12* | $Et_2O$ | 1 | – | 16 | 82 |
| *13* | PhMe | 1 | – | 16 | 69 |
| *14* | $H_2O$ | 1 | – | 24 | 10[e]) |
| *15* | EtOH | 1 | – | 30 | ng |
| *16* | EtOH/$H_2O$ 1:1 | 1 | – | 24 | 15 |
| *17* | $CH_2Cl_2$ | – | – | 24 | nr[f]) |

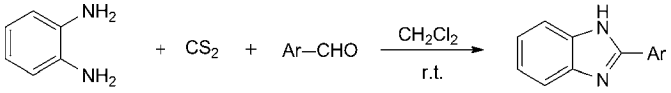
[a]) Yields refer to the isolated pure **5a** as sole product. [b]) ng, Negligible. [c]) The reaction was run in the absence of $CS_2$. After 24 h, the product was not obtained. Then, $CS_2$ (1 mmol) was added, and the reaction was run for an additional 16 h. [d]) The reaction was stopped in mentioned time, and no more product was obtained even after 24 h. [e]) A sticky product was obtained. [f]) nr, No reaction.

We found that up to 94% yield of **5a** was obtained when 1 mmol of $CS_2$ was used (*Entry 5*). This yield decreased by reducing the amount of $CS_2$ down to 0.2 mmol (*Entries 9–11*). One mmol of $CS_2$ was sufficient, and an excess did not increase the yield substantially (*Entries 6–8*). It is known that the solvent plays a crucial factor for organic reactions; so, we examined the reaction in the various solvents (*Table 1*, *Entries 12–16*). The best result was obtained in $CH_2Cl_2$ (*Entry 5*). To establish the crucial role of $CS_2$ as mediator for the synthesis of **5a**, the reaction was examined without $CS_2$ under optimized conditions. It was found that only negligible conversion to **5a** occurred even after 24 h. It indicates that $CS_2$ plays an indispensable role in the formation of **5a** (*Entry 17*).

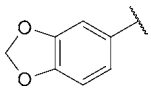
After the optimization of the reaction, the high yield, the simple reaction protocol, and the originality of this efficient process prompted us to explore various aromatic aldehydes (*Scheme 4*). For this purpose, benzene-1,2-diamine (1 mmol) was added to the mixture of arenecarbaldehyde (1 mmol) and $CS_2$ (1 mmol). The resulting mixture was stirred at room temperature in $CH_2Cl_2$. The obtained results are compiled in *Table 2*.

All reactions proceeded efficiently, and the desired products were obtained in good-to-excellent yields in acceptable reaction times without formation of any side-products. Aromatic aldehydes with electron-withdrawing groups (*Table 2*; **5b**, **5e**, **5j**, and **5m**) reacted more efficiently compared with those with electron-releasing groups (*Table 2*;

Table 2. *Synthesis of Benzimidazole Derivatives Using $CS_2$ as Efficient Promoting Medium*




**2** **3a – 3o** **5a – 5o**

| Product | Ar | Time [min] | Yield [%][a]) | M.p. [°] |
|---|---|---|---|---|
| **5a** | Ph | 16 | 91 | 292–293 ([12]: 286–289) |
| **5b** | 4-Cl–$C_6H_4$ | 16 | 92 | 292 ([20a]: 291–293) |
| **5c** | 3-Cl–$C_6H_4$ | 16 | 83 | 229–231 ([20c]: 232–233) |
| **5d** | 2-Cl–$C_6H_4$ | 16 | 82 | 234 ([20b]: 232–234) |
| **5e** | 4-Br–$C_6H_4$ | 16 | 92 | 300–301 ([20c]: 298–299) |
| **5f** | 3-Br–$C_6H_4$ | 16 | 91 | 265–266 ([20a]: 265–266) |
| **5j** | 4-F–$C_6H_4$ | 16 | 93 | 246–248 ([20a]: 245–246) |
| **5h** | 4-Me–$C_6H_4$ | 16 | 87 | 227–229 ([12]: 226–228) |
| **5i** | 4-MeO–$C_6H_4$ | 16 | 77 | 223–224 ([12]: 224–226) |
| **5g** | 2-MeO–$C_6H_4$ | 24 | 42 | 156–158 ([20b]: 157–158) |
| **5k** | 4-$NO_2$–$C_6H_4$ | 16 | 85 | 318–320 ([20c]: 321–322) |
| **5l** | 2-NC–$C_6H_4$ | 16 | 91 | 249–250 ([20c]: 252–253) |
| **5m** | 4-$CF_3$–$C_6H_4$ | 16 | 92 | 266 ([12]: 264–265) |
| **5n** | Furan-2-yl | 16 | 89 | 285–287 ([20b]: 286) |
| **5o** |  | 16 | 75 | 244–245 ([12]: 239–240) |

[a]) Yields refer to the isolated pure product.

**5i** and **5g**). Moreover, our methodology has been used successfully for heteroaromatic aldehydes. The corresponding product was obtained in excellent yield and without any by-product (*Table 2*; **5o**).

Although we have not established the mechanism of the reaction, it should be mentioned that, at the end of reactions, the characteristic smell of $CS_2$ was not recognized. It is also of interest to note that, in the case of 2-aminophenol, the desired product 2-phenyl-1*H*-benzoxazole was not formed. Furthermore, mechanistic investigation on the basis of these observation is currently underway in our laboratory.

In conclusion, we have developed a most practical and reliable procedure for the synthesis of a wide range of 2-substituated 1*H*-benzimidazoles by using inexpensive and readily available starting materials. This method represents a simple and efficient procedure, uses mild reaction conditions, and has general applicability. It avoids toxic catalysts and gives nearly quantitative yields without any by-products. Further exploitation of this methodology is currently underway in our laboratory.

## Experimental Part

*General*. The chemicals were obtained from *Fluka* and *Merck* and were used without purification. M.p.: *Electrothermal 9100* apparatus; uncorrected. IR Spectra: *PerkinElmer Spectrum RXI*. FT-IR apparatus. $^1$H- and $^{13}$C-NMR spectra: *Bruker DRX-300 AVANCE* spectrometer at 250 and 62.5 MHz, resp.; recorded in DMSO with TMS ($Me_4Si$) as internal standard; chemical shifts, $\delta$, in ppm, and $J$ values in Hz. Microanalyses: *PerkinElmer 240-B* microanalyzer.

*(General) Preparation of 2-Phenyl-1*H*-benzimidazole* (**5a**) *in the Presence of $CS_2$.* A mixture of benzene-1,2-diamine (0.108 g, 1 mmol), PhCHO (0.106 g, 1 mmol), and $CS_2$ (0.076 g, 1 mmol) in $CH_2Cl_2$ (2 ml) was stirred in a round-bottom flask at r.t. for 16 h. After completion of the reaction (monitored by TLC AcOEt/hexane 1:1), the precipitate was isolated by filtration and washed with $CH_2Cl_2$ (10 ml) to afford pure **5a** (0.165 g; 91%). White powder. M.p. 291–292° (dec.). (The precipitated products with low purity were further purified by recrystallization from toluene.) IR (KBr): 3397*w*, 2966*m*, 1512*s*, 1269*s*. $^1$H-NMR: 12.89 (br. *s*, NH); 8.16 (*d*, $J$ = 7.9, 2 arom. H); 7.63–7.48 (*m*, 5 arom. H); 7.21–7.19 (*m*, 2 arom. H). $^{13}$C-NMR: 149.9; 144.4; 134.7; 128.8; 128.0; 127.5; 125.7; 123.8; 121.9; 117.6; 113.2. Anal. calc. for $C_{13}H_{10}N_2$ (194.08): C 80.39, H 5.19, N 14.42; found: C 80.31, H 5.23, N 14.51.

*2-(1*H*-Benzimidazol-2-yl)benzonitrile* (**5l**). IR (KBr): 3407*w*, 2317*s*, 1445*s*, 1359*m*. $^1$H-NMR: 13.11 (*s*, NH); 8.10 (*d*, $J$ = 8.1, 2 arom. H); 8.03–7.61 (*m*, 5 arom. H); 7.32–7.28 (*m*, 2 arom. H). $^{13}$C-NMR: 150.6; 148.1; 141.7; 137.9; 135.4; 134.9; 131.2; 128.8; 123.1; 122.6; 121.1; 119.2; 114.7; 111.3. Anal. calc. for $C_{14}H_9N_3$ (219.08): C 76.70, H 4.14, N 19.17; found: C 76.72, H 4.19, N 19.21.

*2-(Furan-2-yl)-1*H*-benzimidazole* (**5n**). IR (KBr): 3449*w*, 1597*s*, 1515*s*, 1109*m*. $^1$H-NMR: 12.91 (*s*, NH); 8.00 (*d*, $J$ = 1.1, 1 arom. H); 7.63–7.61 (*m*, 2 arom. H); 7.27–7.25 (*m*, 2 arom. H); 6.87–6.85 (*m*, 2 arom. H). $^{13}$C-NMR: 145.6; 144.3; 143.7; 121.9; 112.3; 110.6. Anal. calc. for $C_{11}H_8N_2O$ (184.06): C 71.73, H 4.38, N 15.21; found: C 71.72, H 4.41, N 15.18.

*2-(1,3-Benzodioxol-5-yl)-1*H*-benzimidazole* (**5o**). IR (KBr): 3610*w*, 3490*w*, 3026*m*, 2852*m*, 1597*m*, 1464*m*, 1269*s*, 971*s*. $^1$H-NMR: 12.78 (*s*, NH); 7.71–7.68 (*m*, 2 arom. H); 7.59–7.57 (*m*, 2 arom. H); 7.27–7.11 (*m*, 3 arom. H); 6.12 (*s*, $CH_2$). $^{13}$C-NMR: 150.6; 149.3; 147.8; 130.7; 130.1; 125.4; 122.1; 120.9; 110.1; 108.6; 103.4. Anal. calc. for $C_{14}H_{10}N_2O_2$ (238.07): C 70.58, H 4.23, N 11.76; found: C 70.55, H 4.31, N 11.81.

The authors thanks the Islamic Azad University (Shiraz Branch) Research Council and the *Welch Foundation* (Grant A-1656) for support of this work.

## REFERENCES

[1] A. W. Hofmann, *Liebigs Ann. Chem., Suppl.* **1860**, *1*, 1.
[2] T. N. Margulis, D. H. Templeton, *J. Am. Chem. Soc.* **1961**, *83*, 995.

[3] W.-D. Rudorf, *Sulfur Rep.* **1991**, *11*, 51; W.-D. Rudorf, *J. Sulfur Chem.* **2007**, *28*, 295; R. A. Aitken, N. J. Wilson, *Sulfur Rep.* **1998**, *21*, 81.
[4] R. A. Aitken, L. Hill, P. Lightfoot, *Tetrahedron Lett.* **1997**, *38*, 7927; R. A. Aitken, G. Ferguson, S. V. Raut, *J. Chem. Soc., Chem. Commun*. **1991**, 812; N. I. Tyryshkin, I. A. Konovalov, V. V. Gavrilov, N. A. Polezhaeva, *Phosphorus Sulfur Silicon Relat. Elem*. **1996**, *109*, 553.
[5] J.-Y. Wu, Z.-B. Luo, L.-X. Dai, X.-L. Hou, *J. Org. Chem*. **2008**, *73*, 9137; S. Ahadi, G. Hosseini, A. Bazgir, *J. Iran. Chem. Soc.* **2012**, *9*, 333.
[6] N. Azizi, F. Aryanasab, M. R. Saidi, *Org. Lett.* **2006**, *8*, 5275; B. C. Ranu, A. Saha, S. Banerjee, *Eur. J. Org. Chem.* **2008**, 519; B. Karmakar, J. Banerji, *Tetrahedron Lett.* **2011**, *52*, 6584.
[7] I. Yavari, M. Sirouspour, S. Souri, *Monatsh. Chem*. **2010**, *141*, 49; A. Z. Halimehjani, M. H. Shayegan, M. M. Hashemi, N. Notash, *Org. Lett.* **2012**, *14*, 3838.
[8] A. Z. Halimehjani, F. Ebrahimi, N. Azizi, M. R. Saidi, *J. Heterocyclic Chem.* **2009**, *46*, 347.
[9] P. A. Ottersbach, P. W. Elsinghorst, H.-G. Häcker, M. Gütschow, *Org. Lett.* **2010**, *12*, 3662.
[10] J. H. Ryan, C. J. T. Hyland, A. G. Meyer, J. A. Smith, J. Y. Yin, in 'Seven-Membered Rings, Progress in Heterocyclic Chemistry', Eds. G. W. Gribble, J. A. Joule, Elsevier, Oxford, United Kingdom, 2012, p. 493; J. Xu, *Mol. Divers.* **2005**, *9*, 45.
[11] H. R. Safaei, M. Shekouhy, A. Shirinfeshan, S. Rahmanpur, *Mol. Divers.* **2012**, *16*, 669; H. R. Safaei, M. Shekouhy, S. Rahmanpur, A. Shirinfeshan, *Green Chem*. **2012**, *14*, 1696; H. R. Safaei, M. Shekouhy, V. Shafiee, M. Davoodi, *J. Mol. Liq.* **2013**, *180*, 139; H. R. Safaei, M. Davoodi, M. Shekouhy, *Synth. Commun*. **2013**, *43*, 2178; H. R. Safaei, N. Shioukhi, M. Shekouhy, *Monatsh. Chem*. **2013**, *144*, 1855; H. R. Safaei, M. Shekouhy, S. Khademi, V. Rahmanian, M. Safaei, *J. Ind. Eng. Chem*. **2014**, *20*, 3019.
[12] A. J. Blacker, M. M. Farah, M. I. Hall, S. P. Marsden, O. Saidi, J. M. J. Williams, *Org. Lett.* **2009**, *11*, 2039.
[13] F. A. Tanious, D. Hamelberg, C. Bailly, A. Czarny, D. W. Boykin, W. D. Wilson, *J. Am. Chem. Soc*. **2004**, *126*, 143.
[14] I. Yildiz-Oren, I. Yalcin, E. Aki-Sener, N. Ucarturk, *Eur. J. Med. Chem*. **2004**, *39*, 291.
[15] D. J. Sheehan, C. A. Hitchcock, C. M. Sibley, *Clin. Microbiol. Rev.* **1999**, *12*, 40; M. R. Grimmett, in 'Comprehensive Heterocyclic Chemistry II', Eds. A. R. Katrizky, C. W. Rees, E. F. V. Scriven, Vol. 3, Elsevier Science Ltd., Oxford, 1996, Chapt. 3.02; M. R. Grimmett, 'Imidazole and Benzimidazole Synthesis', Academic Press, San Diego, 1997.
[16] V. K. Tandon, M. Kumar, *Tetrahedron Lett.* **2004**, *45*, 4185; R. Trivedi, S. K. De, R. A. Gibbs, *J. Mol. Catal. A: Chem*. **2006**, *245*, 8; M. Curini, F. Epifano, F. Montanari, O. Rosati, S. Taccone, *Synlett* **2004**, 1832; J. B. Wright, *Chem. Rev.* **1951**, *48*, 397; P. N. Preston, *Chem. Rev.* **1974**, *74*, 279; J. M. Smith, J. Gard, W. Cummings, A. Kanizsai, V. Krchňák, *J. Comb. Chem.* **1999**, *1*, 368; D. Tumelty, K. Cao, C. P. Holmes, *Org. Lett*. **2001**, *3*, 83; M. Chakrabarty, S. Karmakar, A. Mukherji, S. Arima, Y. Harigaya, *Heterocycles* **2006**, *68*, 967; K. Bahrami, M. M. Khodaei, I. Kavianinia, *Synthesis* **2007**, 547; H. Aliyan, R. Fazaeli, N. Fazaeli, A. R. Mssah, H. J. Naghash, M. Alizadeh, G. Emami, *Heteroatom Chem.* **2009**, *20*, 202; Z.-H. Zhang, L.Yin, Y.-M. Wang, *Catal. Commun*. **2007**, *8*, 1126.
[17] K. Nagata, T. Itoh, H. Ishikawa, A. Ohsawa, *Heterocycles* **2003**, *61*, 93; R. Wang, X.-X. Lu, X.-Q. Yu, L. Shi, Y. Sun, *J. Mol. Catal. A: Chem*. **2007**, *266*, 198; A. Dhakshinamoorthy, K. Pitchumani, *Catal. Commun.* **2009**, *10*, 872.
[18] X. Lv, W. Bao, *J. Org. Chem*. **2009**, *74*, 5618; J. Peng, M. Ye, C. Zong, F. Hu, L. Feng, X. Wang, Y. Wang, C. Chen, *J. Org. Chem*. **2011**, *76*, 716; X. Deng, H. McAllister, N. S. Mani, *J. Org. Chem*. **2009**, *74*, 5742.
[19] M. Belaud-Rotureau, T. T. Le, T. H. T. Phan, T. H. Nguyen, R. Aissaoui, F. Gohier, A. Derdour, A. Nourry, A.-S. Castanet, K. P. P. Nguyen, J. Mortier, *Org. Lett.* **2010**, *12*, 2406.
[20] a) H. G. Charansingh, S. J. Ratnadeep, G. M. Priyanka, K. D. Sanjay, *J. Chin. Chem. Soc.* **2010**, *57*, 1227; b) L.-H. Du, X.-P. Luo, *Synth. Commun.* **2010**, *40*, 2880; c) M. Shen, T. G. Driver, *Org. Lett.* **2008**, *10*, 3367.

*Received January 21, 2014*