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ISSN: 2231 – 3087(print) / 2230 – 9632 (Online)
Vol. 1: (4), 2011, 365-371

THE SYNTHESIS OF IMIDAZOLES VIA THE RADZISZEWSKI REACTION IN AQUEOUS MEDIA

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Abstract: A new, simple and eco-friendly protocol has been developed for the preparation of trisubstituted imidazoles through the Radziszewski reaction between formaldehyde (37% aqueous solution), amines, ammonium carbonate and biacetyl. The synthesis was conductedat room temperature using water as the solvent.

Keywords: Imidazole, Radziszewski Reaction, Water, Green Chemistry

1. Introduction

Heterocyclic chemistry is an important subfield of synthetic organic chemistry that encompasses a wide variety of potent molecules[1]. Imidazole derivatives occupy a special place in organic and medicinal chemistry[2] because these compounds are found as scaffolds in many significant biomolecules[3], including the essential amino acid histidine, histamine and pilocarpina alkaloids[4], inhibitors of P38 MAP kinase[5], and plant growth regulators[6].They are also used as fungicides and herbicides[7]. Compounds with the imidazole ring have many pharmaceutically useful properties, such as anti-inflammatory[8], anti-allergic[9], anti-microbial[10], anti-tubercular[11] and analgesic activities[12]. Several marketed drugs contain the imidazole framework, including losartan, cimetidine and eprosartan[13].Numerous applications in organometallic catalysis, coordination chemistry and green chemistry have also extended of the use of imidazole derivatives to the synthesis and application of ionic liquids[14] and stable N-heterocyclic carbenes[15].

There are several methods reported in the literature for the synthesis of imidazoles, such as the reaction of *N*-(2-oxo)-amides with ammonium trifluoroacetate[16], hetero-Cope rearrangement[17], condensation of β-carbonyl-*N*-acyl-*N*-alkylamines with ammonium acetate in refluxing acetic acid[18], four component condensation of arylglyoxals, primary amines, carboxylic acids and isocyanides on Wang resin[19], treating 1,2-aminoalcohols with PCl_5[20],palladium-catalyzed cyclization of *O*-pentafluorobenzoylamidoximes[21],copper-catalyzed cross-cycloaddition between isocyanides[22],reacting keto-oximes and aldehydes with ammonium acetate[23] and α-aminonitriles with Vilsmeier reagent[24].

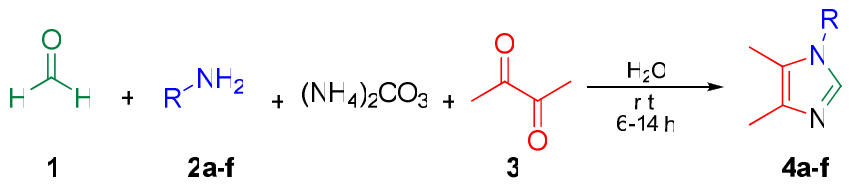
However, many of the synthetic protocols for the preparation of imidazoles reported above suffer from one or more disadvantages, such as harsh reaction conditions, organic solvents (MeOH, EtOH, DMF, DMSO)and expensive catalysts.

The most convergent method for the preparation of highly substituted imidazoles is the Radziszewski reaction[25] reported in 1882. In the original reaction, a diketone and an aldehyde reacted with excess NH_3 in a one-pot process to give the corresponding imidazole. Recently,several modifications for the Radziszewski reaction have been developed for the syntheses of 1,2,4,5-tetrasubstituted imidazoles and 2,4,5-trisubstituted imidazoles.Many of these reactions involve exposing 1,2-diketones and aldehydes to a variety of calalysts, such as molecular iodine[26], $NiCl_2.6H_2O$[27], heteropolyacids[28], L-proline[29].Microwave-assisted reactions conditions have also been widely used to construct these scaffolds, including MW/silica-gel/$HClO_4$[30], MW/silica-gel/$NaHSO_4$[31], MW/zeolite HY[32], MW/Al_2O_3[33], MW/acetic acid[34], and MW/SSA[35].However, these methods are limited by their use of high temperatures, corrosive reagents, and expensive instruments such asmicrowave reactors.

2. Results and Discussion

The creation of newsynthetic protocols that explorea diversity of starting materials without ignoring economic and environmental aspects constitutes a great challenge in modern organic chemistry from both academic and industrial perspectives[36]. In this context, the use of multicomponent reactions in organic syntheses is highly desirable[37]. Additionally, the use of non-organic solvents for chemical synthesis is important in the drive toward benign chemical technologies. Organic solvents are high on the list of toxic or otherwise damaging substances because of the large volumes used in industry and the difficulty of containing volatile compounds[38].

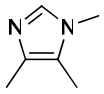
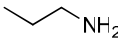
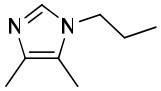
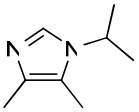
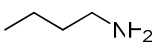
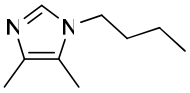
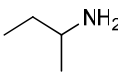
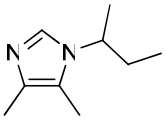
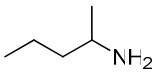
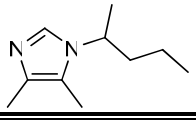
In the continuation of our studies toward the development of new green chemistry methodologies[39], we reporthereinthe formation of imidazoles **4a-f**via a modification of the Radziszewski synthesis that makes use of formaldehyde **1**, several commercially availablealiphatic amines **2a-f**,biacetyl **3**and ammonium carbonate as a source of nitrogen. These reactions wereconductedat room temperature in a one-pot process using water as the solvent (Scheme 1). The products wereobtained with acceptable yields (13-24%) (Table 1).



1 2a-f 3 4a-f

Scheme 1. Synthesis of 1,4,5-trisubstituted imidazoles in aqueous media.

Table 1. Synthesis of 1,4,5-trisubstituted imidazoles in aqueous media

Entry	Comp.	Amine	Imidazole	Time (h)	Yield* (%)	Lit. (%)
1	**4a**			6	13	60[a]
2	**4b**			6	24	---
3	**4c**			6	15	15[b]
4	**4d**			6	22	73[c]
5	**4e**			6	22	---
6	**4f**			14	21	---

*Isolated Yield
[a]Conditions: 15 h of reaction, solvent MeOH[40]
[b]Conversion basedon ^{1}H NMR[34]
[c]Two steps from the N-oxide substrate[41]

Imidazoles **4a**and**4d**have been previously synthesized using different methods that resulted in higher overall yields. However, the downside of these approaches is that they often require hazardous conditions, toxic organic solvents, expensive catalysts and multi-step procedures.

The above methodology has a wide scope and allows for good structural diversification of the imidazole ring, supplying the possibility of subsequent chemical transformations for the synthesis of more complex molecules. This protocol not only affords the pure products but also avoids the problems associated with residues, organic solvents, handling, safety and pollution. Water can act as an eco-friendly solvent for a variety of organic transformations. It is recyclable, non-explosive, inexpensive and easy to handle.

3. Experimental Section

Materials and Methods

IR spectra were obtained on a Nicolet Magna IR-FT spectrometer withKBr film. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 500 spectrometer (500 MHz ^{1}H NMR and 125 MHz ^{13}C NMR) with a FT-NMR system. Data for ^{1}H NMR are reported as chemical shift (δ) and

multiplicity (s: singlet, d: doublet, t: triplet, quint: quintuplet, sex: sextuplet,sep: septuplet,dquint: doublet of quintuplet, m: multiplet). GLC analyses were performed on a GC-2010 Shimadzu Corporation FID instrument equipped with a 30m x 0.5μm DB-5ms capillary column. Mass spectra were recorded with a mass selective detector (Shimadzu Corporation QP2010S) interfaced to a capillary gas chromatograph. All reagents were purchased from TCI America and Spectrum Co. The spectral data of known compounds were in accordance with those reported.

*General experimental procedure for the synthesis of 1,4,5-trisubstituted imidazoles**4a-f**:*

A mixture of formaldehyde (37% aqueous solution)**1** (50 mmol), primary amine **2b-f** (50 mmol), ammonium carbonate (25 mmol) and biacetyl (50 mmol) in 10 mL waterwas stirred at room temperature for the time listed in Table 1. In the case of methylamine**2a**(40% aqueous solution), 4.0 mL of methylamine solution and 7.5 mL of water were used.Reaction progress was monitored by high-resolution GC. After completion of the reaction, the reaction mixture was extracted with dichloromethane (3x20 mL), dried over Na_2SO_4 and evaporated under reduced pressure. The crude products **4a-f**werepurified by distillation under reduced pressure.

1,4,5-trimethyl-1*H*-imidazole (4a): R_f : 0.24 (1:1 *n*-hexane:acetone); bp. 88°C/7 mmHg.**IR** (KBr): 3106 $\nu_{(CH)}$, 2919 and 2863 $\nu_{(Me)}$, 1670 $\nu_{(C=C),}$ 1506 $\nu_{(C=N)}$, 1232 $\nu_{(C-N)}$ cm^{-1}.**^{1}H NMR** (400 MHz, $CDCl_3$) δ: 2.09 (3H, s), 2.13 (3H, s), 3.47 (3H, s),7.25 (3H, s).**^{13}C NMR**(100 MHz, $CDCl_3$) δ: 7.8, 12.3, 31.0, 122.3, 133.1,134.9.**GC-MS**: R_t: 8.8 min.; *m*/z (%): 110 ($M^{+\cdot}$, 100), 109 (88), 95 (35), 82 (5), 68 (25), 56 (24), 42 (29).

4,5-dimethyl-1-propyl-1*H*-imidazole (4b): R_f: 0.45 (1:1 *n*-hexane:acetone); bp. 123°C/15 mmHg.**IR** (KBr): 3108 $\nu_{(CH)}$, 2966 and 2877 $\nu_{(Me)}$, 2933 $\nu_{(CH_2)}$, 1664 $\nu_{(C=C),}$ 1502 $\nu_{(C=N)}$, 1241 $\nu_{(C-N)}$ cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 0.92 (3H, t, *J* = 7.4 Hz), 1.71 (2H, sex, *J* = 7.3 Hz), 2.11 (3H, s), 2.14 (3H, s), 3.73 (2H, t, *J* = 7.2 Hz),7.31 (1H, s). **^{13}C NMR**(100 MHz, $CDCl_3$) δ: 8.1, 10.8, 12.4, 23.8, 46.3, 121.7, 133.2,134.5. **GC-MS**: R_t: 11.0 min.; *m*/z (%): 138 ($M^{+\cdot}$, 100), 123 (11), 109 (30), 95 (53), 81 (15), 69 (23), 55 (14), 41 (20).

1-*iso*-propyl-4,5-dimethyl-1*H*-imidazole (4c): R_f: 0.42 (1:1 *n*-hexane:acetone); bp. 110°C/11 mmHg.**IR** (KBr): 3110 $\nu_{(CH)}$, 2977 and 2875 $\nu_{(Me)}$, 1668 $\nu_{(C=C),}$ 1492 $\nu_{(C=N)}$, 1226 $\nu_{(C-N)}$ cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 1.44 (6H, d, *J* = 6.7 Hz), 2.13 (3H,s), 2.15 (3H, s), 4.15 (1H, sep, *J* = 6.7 Hz),7.41 (1H, s). **^{13}C NMR**(100 MHz, $CDCl_3$) δ: 8.4, 12.4, 23.1, 46.6, 121.3, 131.3,133.2. **GC-MS**: R_t: 10.6 min.;*m*/z (%): 138 ($M^{+\cdot}$, 66), 123 (6), 95 (100), 81 (28), 68 (4), 54 (9), 41 (12).

1-butyl-4,5-dimethyl-1*H*-imidazole (4d): R_f: 0.50 (1:1 *n*-hexane:acetone); bp. 134°C/13 mmHg.**IR** (KBr): 3102 $\nu_{(CH)}$, 2958 and 2873 $\nu_{(Me)}$, 2933 $\nu_{(CH_2)}$, 1670 $\nu_{(C=C),}$ 1500 $\nu_{(C=N)}$, 1234 $\nu_{(C-N)}$ cm^{-1}.**^{1}H NMR** (500 MHz, $CDCl_3$) δ: 0.94 (3H, t, *J* = 7.3Hz), 1.33 (2H, sex, *J* = 7.4 Hz), 1.66 (2H, quint, *J* = 7.4 Hz), 2.11 (3H, s), 2.15 (3H, s), 3.76 (2H, t, *J* = 7.2 Hz),7.29 (1H, s). **^{13}C NMR**(100 MHz, $CDCl_3$) δ: 8.2, 12.5, 13.3, 19.5, 32.6, 44.4, 121.6, 133.4,134.5. **GC-MS**: R_t: 12.4 min.;*m*/z (%): 152 ($M^{+\cdot}$, 100), 137 (21), 123 (6), 110 (77), 95 (55), 83 (23), 69 (54), 55 (18), 42 (24).

1-(*sec*-butyl)-4,5-dimethyl-1*H*-imidazole (4e): R_f: 0.47 (1:1 *n*-hexane:acetone); bp. 115°C/9 mmHg.**IR** (KBr): 3104 $\nu_{(CH)}$, 2969 and 2875 $\nu_{(Me)}$, 2931 $\nu_{(CH_2)}$, 1668 $\nu_{(C=C)}$, 1492 $\nu_{(C=N)}$, 1222 $\nu_{(C-N)}$ cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 0.86 (3H, t, *J* = 7.4 Hz), 1.42 (3H, d, *J* = 6.8 Hz), 1.74 (1H, dquint, *J* = 14.8,7.2 Hz), 1.79 (1H, dquint, *J* = 14.8, 7.2 Hz), 2.11 (3H, s), 2.16 (3H, s), 3.90 (1H, sex, *J* = 6.8 Hz),7.37 (1H, s). **^{13}C NMR**(100 MHz, $CDCl_3$) δ: 8.8, 10.6, 12.6, 21.4, 30.4, 52.6, 121.7, 132.1,133.2.**GC-MS**: R_t: 10.9 min.; *m*/z (%): 152 ($M^{+\bullet}$, 55), 137 (2), 123 (16), 96 (48), 95 (100), 81 (31), 68 (4), 54 (11), 41 (25).

4,5-dimethyl-1-(pentan-2-yl)-1*H*-imidazole (4f): R_f : 0.57 (1:1 *n*-hexane:acetone); bp. 130°C/12 mmHg.**IR** (KBr): 3106 $\nu_{(CH)}$, 2962 and 2871 $\nu_{(Me)}$, 2931 $\nu_{(CH_2)}$, 1666 $\nu_{(C=C)}$, 1492 $\nu_{(C=N)}$, 1218 $\nu_{(C-N)}$ cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 0.90 (3H, t,*J* = 7.4 Hz), 1.19-1.33 (2H, m), 1.42 (3H, d, *J* = 6.8 Hz), 1.64-1.80 (2H, m), 2.11 (3H, s), 2.15 (3H, s), 3.98 (1H,sex, *J* = 6.9 Hz),7.37 (1H, s). **^{13}C NMR**(100 MHz, $CDCl_3$) δ: 8.9, 12.7, 13.7, 19.4, 22.0, 39.7, 51.0, 121.7, 132.1,133.2.**GC-MS**: R_t: 12.2 min.;*m*/z (%): 166 ($M^{+\bullet}$, 44), 151 (9), 124 (34), 110 (10), 95 (100), 81 (28), 68 (5), 55 (14), 43 (43).

4. Conclusion

We have developed an eco-friendly, one-pot synthesis of 1,4,5-trisubstituted imidazoles by the cyclocondensation of formaldehyde, ammonium carbonate and biacetylwith several different amines. This novel protocol offers notable merits, such as mild reaction conditions, simple procedure, short reaction time, acceptable yields and a good entry to a range of imidazoles.

Acknowledgments

We gratefully acknowledge Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (Capes) for financial support (a fellowship to J. A. H. M.).

5. References

1. S. N. Murthy, B. Madhav, Y. V. D. Nageswar, Tetrahedron Lett. 51, 5252, (2010)
2. (a) B. H. Lipshutz, Chem. Rev. 86, 795 (1986); (b) A. P. Pozharskii, A. D. Garnovskii, A. M. Simonov, Russ. Chem. Rev. 35, 122 (1966) (c) J. L. Adams, J. C. Boehm, S. Kassis, P. D. Gorycki, E. F. Webb, R. Hall, M. Sorenson, J. C. Lee, A. Ayrton, D. E. Griswold, T. F. Gallagher, Bioorg. Med. Chem. Lett. 8, 3111 (1998); (d) J. G. Lombardino, E. H. Wiseman, J. Med. Chem 17, 1182 (1974); (e) J. G. Lombardino, Chem. Abstr, 77, 1016074 (1972)(f) Y. S. Lo, J. C. Nolan, T. H. Maren, W. J. Jr. Welstead, D. F. Gripshover, D. A. Shamblee, J. Med. Chem. 35, 4790 (1992)
3. (a) H. B. Sun, G. J. Zheng, Y. P. Wang, X. J. Wang, W. S. Xiang, Chin.Chem. Lett. 20, 269, (2009); (b) S. C. Shilcrat, M. K. Mokhallalati, J. M. D. Fortunak, L. N. Pridgen, J. Org. Chem. 62, 8449 (1997); (c)M. R. Grimmett, in: Comprehensive Hetrocyclic Chemistry, A. R. Katritzky, C. W. Rees (Eds.), vol. 5, Pergamon, New York, p. 374; (1984); (d) M. R. Grimmett, in: Comprehensive Hetrocyclic Chemistry II, A. R. Katritzky, C. W. Rees, E. F. V. Scriven (Eds.), vol. 3, Pergamon, New York, p. 77; (1996)
4. (a) A. P. Santos, P. R. H.; Moreno, Braz. J. Pharm. Sci. 40, 115 (2004); (b) A. P. Higson, A. Hamer, Speciality Non-food Crops. In: Plant-derived Natural Products Synthesis, Function, and Application. A. E. Osbourn, V. Lanzotti, Springer. 571 (2009); (c) Y. S.

Lo, J. C. Nolan, T. H. Maren, W. J. Welstead, D. F. Gripshover, D. A. Shamblee, J. Med. Chem. 35,4790 (1992)
5. (a) J. C. Lee, J. T. Laydon, P. C. McDonnell, T. F. Gallagher, S. Kumar, D, Green, D. McNulty, M. J. Blumenthal, J. R. Keys, S. W. L. Vatter, J. E. Strickler, M. M. McLaughlin, I. R. Siemens, S. M. Fisher, G. P. Livi, J. R. White, J. L. Adams, P. R. Young, Nature, 372, 739 (1994) (b) R. Kitbunnadaj, O. P. Zuiderveld, B. Christophe, S. Hulscher, W. M. P. B. Menge, E. Gelens, E. Snip, R. A.Bakker, S. Celanire, M. Gillard, P. Talaga, H. Timmerman, R. Leurs, J. Med. Chem. 10, 2414 (2004); (c) J. L. Adams, J. C. Boehm, T. F. Gallagher, S. Kassis, E. F. Webb, R. Hall, M. Sorenson, R. Garigipati, D. E. Griswold, J.C. Lee, Bioog. Med. Chem. Lett. 11, 2867 (2001)
6. (a) R. Shmierer, H. Mildenberger, H. Buerstell, German Patent 3614354 (1987); (b) R. Shmierer, H. Mildenberger, H. Buerstell, Chem. Abstr. 108 (1988)
7. (a) T. Maier, R. Schmierer, K. Bauer, H. Bieringer, H. Buerstell, B. Sachser, German Patent 317094 (1983); (b) T. Maier, R. Schmierer, K. Bauer, H. Bieringer, H. Buerstell, B. Sachser, Chem. Abstr. 100, (1984) 85699; (c) T. Maier, R. Schmierer, K. Bauer, H. Bieringer, H. Buerstell, B. Sachser, US Patent 4820335 (1989)
8. (a) K. Khanna, R. M. Weier, Y. Yu, X. D. Xu, F. J. Koszyk, P. W. Collins, C. M. Koboldt, A. W. Veehuizen, W. E. Perkins, J. J. Casler, J. L. Masferrer, Y. Y. Zhanf, S. A. Gregory, K. Seibert, P. C. Isakson, J. Med. Chem. 40, 1634 (1997); (b) A. Puratchikody, M. Doble, Bioorg. Med. Chem. 15, 1083 (2007) (c) T. F. Gallagher, S. M. Fier-Thompson, R. S. Garifipati, M. E. Sorenson, J. M. Smietana, D. Lee, P. E. Bender, J. C. Lee, J. T. Laydon, D. E. Griswold, M. C. Chabot-Fletcher, J. J. Breton, J. L. Adams, Bioorg. Med. Chem. Lett. 5, 1171 (1995)
9. J. W. Black, G. J. Durant, J. C. Emmett, C. R. Ganellin, Nature, 248, 65 (1974)
10. (a) A. Ejima, T. Hayano, T. Ebata, T. Hagahara, H. Koda, H. Tagawa, M. Furukawa, J. Antibiot. 40, 43 (1987); (b) D. Sharma, B. Narasimhan, P. Kumar, V. Judge, R. Narang, E. De Clercq, J. Balzarini, Eur. J. Med. Chem. 44, 2347 (2009) (c) T. Uno, M. Takamatsu, Y. Inoue, Y. Kawahata, K. Iuchi, G. Tsukamoto, J. Med. Chem. 30,2163 (1987)
11. (a) P. Gupta, S. Hameed, R. Jain, Eur. J. Med. Chem. 39, 805 (2004); (b) J. Pandey, V. K. Tiwari, S. S. Verma, V. Chaturvedi, S. Bhatnagar, S. Sinha, A.N. Gaikwad, R. P. Tripathi, Eur. J. Med. Chem. 44, 3350 (2009)
12. Ü. Uçucu, N. G. Karabunrun, I. Isikdag, II Farmaco, 56, 285 (2001)
13. (a) P. Lindberg, P. Nordberg, T. Alminger, A. Braendstroem, B. Wallmark, 29, 1327 (1986); (b) S. E. Wolkenberg, D. D. Wisnoski, W. H. Leister, Y. Wang, Z. Zhao, C. W. Lindsley, Org. Lett. 6, 1453 (2004); (c) S.L. Abrahams, R.J. Hazen, A.G. Batson, A.P. Phillips, J. Pharmacol. Exp. Ther. 249, 359 (1989) (d) M. McIntrye, S. E. Caffe, R. A. Michalak, J. L. Reid, Pharmacol. Ther. 74 181 (1997)
14. (a) T. Welton, Chem. Rev. 99, 2071 (1999); (b) P. Wasserscheid, W. Keim, Angew. Chem., Int. Ed. 39, 3772 (2000); (c) R. Sheldon, Chem. Commun. 2399 (2001)
15. (a) W. A. Herrmann, Angew. Chem., Int. Ed. 41, 1290 (2002); (b) V. César, S. Bellemin-Laponnaz, L. H. Gade, Chem. Soc. Rev. 33, 619 (2004); M. Heckenroth, A. Neels, M. G. Garnier, P. Aebi, A. W. Ehlers, M. Alberecht, Chem. Eur. J. 15, 9375 (2009)
16. C.F. Claiborne, N.J. Liverton, K.T. Nguyen, Tetrahedron Lett. 39,8939 (1998)
17. I. Lantos, W. Y. Zanng, Y. Shiu, D. S. Eggleston, J. Org. Chem. 58, 7092 (1993)
18. D.A. Evans, K.M. Lundy, J. Am. Chem. Soc. 114, 1495 (1992)

19. C. Zhang, E. J. Moran, T. F. Woiwade, K. M. Short, A. M. M. Mjalli, Tetrahedron Lett. 37, 751 (1996)
20. (a) C. F. Claiborne, N. J. Liverlon, K. T. Nguyen, Tetrahedron Lett. 39, 8939 (1998); (b) K. H. Bleicher, F. Gerber, Y. Wüthrich, A. Alanine, A. Capretta, Tetrahedron Lett. 43, 7687 (2002) (PCl5)
21. (a) A. R. Siamaki, B. A. Arndtsen, J. Am. Chem. Soc. 128, 6050 (2006); (b) S. Zaman, K. Mitsuru, A. D. Abell, Org. Lett. 7, 609 (2005)
22. C. Kanazawa, S. Kamijo, Y. Yamamoto, J. Am. Chem. Soc. 128, 10662 (2006)
23. R. B. Sparks, A. P. Combs, Org. Lett. 6, 2473 (2004)
24. V. G. Pawar, W. M. De Borggraeve, K. Robeyns, L. V. Meervelt, F. Compernolle, G. Hoornaert. Tetrahedron Lett. 47, 5451 (2006)
25. B. Radziszewski, Chem. Ber. 15, 1493 (1882)
26. M. Kidwai, P. Mothsra, V. Bansal, R. K. Somvanshi, A. S. Ethavathulla, S. Dey. T. P. Singh, J. Mol. Catal. A. Chem. 265, 177 (2007)
27. M. M. Heravi, K. Bakhtiari, H. A. Oskooie, S. Taheri, J. Mol. Catal. A Chem. 263, 279 (2007)
28. (a) M. M. Heravi, F. Derikvand, F. F. Bamoharram, J. Mol. Catal. A Chem. 263, 112 (2007; (b) A. R. Karimi, Z. Alimohammadi, M. M. Amini, Mol. Divers. 14, 635 (2010)
29. S. Samai, G. C. Nandi, P. Singh, M.S. Singh, Tetrahedron 65, 10155 (2009)
30. S. Kantevari, S. V.N. Vuppalapati, D. O. Biradar, L. Nagarapu, J. Mol. Catal. A Chem. 266, 109 (2007)
31. (a) A. R. Karimi, Z. Alimohammadi, J. Azizian, A. A. Mohammadi, M. R. Mohammadizadeh, Catal. Commun. 7, 728 (2006); (b) H. A. Oskooie, Z. Alimohammadi, M. M. Heravi, Heteroatom. Chem. 17, 699 (2006)
32. (a) S. Balalaie, A. Arabanian, Green Chem. 2, 274 (2000); (b) S. Balalaie, A. Arabanian, M. S. Hashtroudi, Monatsh. Chem., 131, 945 (2000); (c) K. Sivakumar, A. Kathirvel, A. Lalitha, Tetrahedron Letters. 51, 3018 (2010)
33. A. Y. Usyatinsky, Y. L. Khmelnitsky, Tetrahedron Letters. 41, 5031 (2000)
34. E. Gelens, F. J. J. De Kanter, R. F. Schmitz, L. A. J. M. Sliedregt, B. J. V. Steen, C. G. Kruse, R. Leurs, M. B. Groen, R. V. A. Orru, Mol. Divers. 10, 17 (2006)
35. (a) A. Shaabani, A. Rahmati, E. Farhangi, Z. Badri, Catal. Commun. 8, 1149 (2007); (b)A. Shaabani, A. Rahmati, J. Mol. Catal. A Chem.249, 246 (2006)
36. A. Lubineau, J. Augé, Topics in Current Chemistry, 206, 1 (1999)
37. A. Dömling, Chem. Rev. 106, 17 (2006)
38. G.W.V. Cave, C.L. Raston, J.L. Scott, Chem. Commun. 37, 2159 (2001)
39. (a) J. S. Bello Forero, E. M. de Carvalho, J. Jones Jr, F. M. da Silva, Heterocyclic Lett. 1, 61, (2011); (b) F. M. da Silva, P. S. B. de Lacerda, J. Jones Jr, Quim. Nov**a**28, 103 (2005); (c) F. M. da Silva, J. Jones Jr, Quim. Nova24, 646 (2001); (d) F. M. da Silva, J. Jones Jr, J. Braz. Chem. Soc.12, 135 (2001); (e) F. M. da Silva, J. Jones Jr, Can. J. Chem.77, 624 (1999)
40. A. J. Arduengo, F. P. Gentry, P. K. Tavekere,. US Patent. 6177575,(2001)
41. G. Mloston, J. Romanski, M. Jasinki, H. Heimgartner, Tetrahedron: Asymmetry. 20, 1073 (2009)

Received on July 15, 2011.