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Lewis acid catalyst free synthesis of benzimidazoles and formamidines in 1,1,1,3,3,3-hexafluoro-2-propanol

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ABSTRACT

A simple, inexpensive, environmentally friendly and efficient route for the synthesis of benzimidazole and formamidine derivatives by the reaction of *O*-phenylenediamines or amines with orthoesters using hexafluoroisopropanol as a solvent/catalyst is described.

1. Introduction

Over the last years, fluorinated alcohols have, due to their unique chemical and physical properties, attracted an increasing interest in the context of green reaction media, as co-solvent or additive [1]. Highly fluorinated alcohols exhibit high hydrogen bonding donor ability, low nucleophilicity, high ionizing power and the ability to solvate water. Reactions in fluorinated alcohols are generally selective and without effluents, allowing thus a facile isolation of the product and can be easily recovered by distillation. Among several of fluorinated alcohols, the most commonly used and cheapest are trifluoroethanol (TFE) and hexafluoroisopropanol (HFIP), which are available on a commercial scale. Due to their use in solvolysis reaction, where the generated cationic intermediates, can be trapped by nucleophiles [2] and their interaction with acetals to form the electrophilic species [3], it could be anticipated that these solvents could be useful as a medium for activation of orthoesters. In continuation of our interest using of fluorinated solvents as efficient medium in various organic transformations [4], we reasoned that it could assist certain condensation reactions. In this report we describe our results for the synthesis of Benzimidazoles. These heterocycles are very important compounds which show a broad range of biological activities such as antiviral, antihypertension, anticancer properties [5,6] and express significant activity against several viruses such as HIV [7], Herpes (HSV-1) [8], human cytomegalovirus (HCMV) [9] and influenza [10]. They have also been used as ligands for asymmetric transformations [11]. According to the literature, benzimidazoles were typically synthesized by the reaction of an appropriate substituted 1,2-phenylenediamine with carboxylic acid or its derivatives [12], nitriles [13], and orthoesters [14] in the presence of a strong acid at elevated temperature. Recently, several methods have been introduced, where aldehydes [15], acid chlorides [16], *O*-dinitrobenzene [17], Gold's reagent [18] and 2-nitroanilines [19] were used as starting materials for this synthesis. However, some of these methods suffer from one or more of the following drawbacks such as strong acidic conditions, long reaction times, low yields of the products, tedious work-up, need to excess amounts of reagent and the use of toxic reagents, catalysts and/or solvents. Therefore, there is a strong demand for a highly efficient and environmentally benign method to prepare these heterocycles. The present investigation describes a facile preparation of benzimidazole derivatives from *O*-phenylenediamines and orthoesters in HFIP (Scheme 1).

2. Results and discussion

In preliminary experiments, *O*-phenylenediamine (1 mmol) in 1 mL TFE was allowed to stir at room temperature with trimethylorthoformate. After 10 h, only 30% of expected benzimidazole **1a** was obtained. Our efforts were then focused on HFIP.

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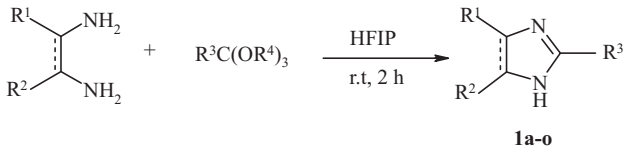


1a-o

Scheme 1.

As a strong H-bond donor (α = 1.96, pK_a = 9.3), with high ionizing power (Y_{OTs} = 3.79), and polarity (P_s = 11.08), it could activate the orthoesters towards the nucleophilic attack of amine groups. The reaction was then investigated in HFIP: where a solution of *O*-phenylenediamine (1 mmol), trimethylorthoformate (1 mmol) in HFIP (Table 1, entry **1**) was stirred at room temperature. The reaction was remarkably fast (2 h) and, after distilling off the HFIP, the benzimidazole **1a** was isolated in 95% yield. Further experiments revealed that a similar procedure is applicable for the preparation of a wide range of compounds analogous to adduct **1** (Table 1). The study was extended to aromatic (entries **1**–**11**), aliphatic (entries **12** and **13**), and heterocyclic diamines (entries **14** and **15**) furnishing the products by a smooth cyclocondensation within 2 h. The yields in general are high, regardless of the structural variations of the diamines.

The syntheses of amidines have in recent years received significant attention. This is because of their wide range of biological [20] and pharmaceutical activities [21] such as histamine-receptor antagonists [22], serine-protease inhibitors [23] and nitric oxide synthase inhibitors [24]. Furthermore, these compounds can be used as pesticides and acaricides [25], analgesic [24], antibacterial and antipyretic [26]. Moreover, substituted amidines are valuable synthon in the synthesis of many azacyclic compounds [27]. The amidine group was also found to be *an* effective protecting group for primary amines [28], electrophiles [29], nitrogen-based nucleophile [30], auxiliaries [31] and a linker in solid-phase synthesis [32]. Classical method for the synthesis of amidine derivatives is the condensation of amines with orthoesters using organic and mineral acids under rather forcing conditions [33]. Numerous variations of procedures have been reported in the literature. These include the nucleophilic addition of amines to nitriles (the most convenient and atom-economic method) [34], condensation reactions of amines with activated amide intermediates, e.g. imino esters [35], imidoyl chlorides [36] or *O*-triflated imidates [37], thioamides [38], carboxylic acids [39], carboxylic esters [40], orthoesters [41] as a solvent and a reagent in the presence of condensation agents and Beckman-type rearrangement of ketoximes [42]. In addition, formamidines are usually formed by the condensation of primary

Table 1
Synthesis of benzoimidazole derivatives in HFIP.

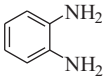
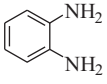
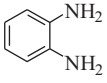
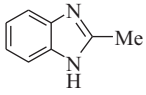
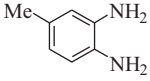
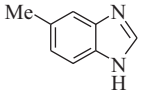
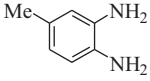
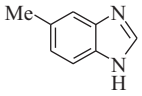
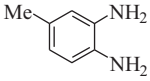
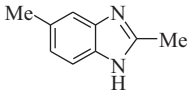
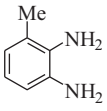
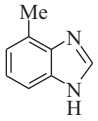
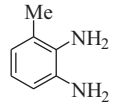
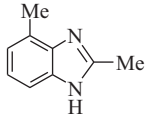
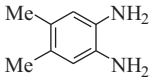
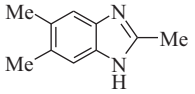
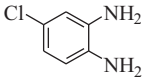
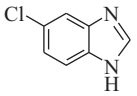
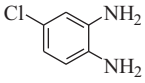
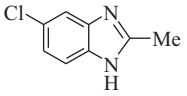
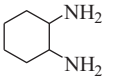
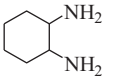
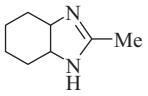
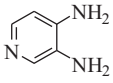
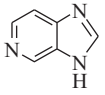
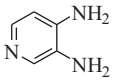
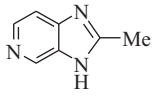
Entry	Diamine	Ortho-ester	Product		Yield (%)
1		$CH(OMe)_3$		**1a**	95
2		$CH(OEt)_3$		**1b**	92
3		$CH_3CH(OMe)_3$		**1c**	92
4		$CH(OMe)_3$		**1d**	92
5		$CH(OEt)_3$		**1e**	90
6		$CH_3CH(OMe)_3$		**1f**	90
7		$CH(OMe)_3$		**1g**	90

Table 1 (*Continued*)

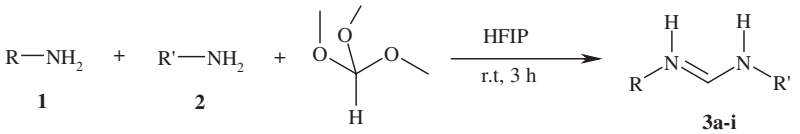
Entry	Diamine	Ortho-ester	Product		Yield (%)
8		$CH_3CH(OMe)_3$		**1h**	90
9		$CH_3CH(OMe)_3$		**1i**	92
10		$CH(OMe)_3$		**1j**	85
11		$CH_3CH(OMe)_3$		**1k**	88
12		$CH(OMe)_3$		**1l**	90
13		$CH_3CH(OMe)_3$		**1m**	90
14		$CH(OMe)_3$		**1n**	85
15		$CH_3CH(OMe)_3$		**1o**	88

amines and *N*,*N*-dialkylformamide dimethylacetals under neutral conditions [43]. Recently, Lin et al. demonstrated that sulfated zirconia catalyzed the reaction between aniline and trimethylorthoformate to produce formamidine at 40 °C [44]. In fact, formamidines are known [45] to be particularly unstable under many of the conditions encountered during their purification steps. These factors make the trans-amidination of *N*,*N*-dimethyl formamidines a very attractive synthetic route for the preparation of N^2,N^3-unsymmetrical formamidines, but are not suitable for a combinatorial approach or for high throughput synthesis.

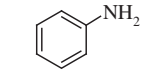
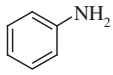
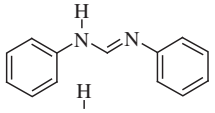
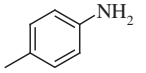
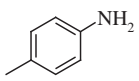
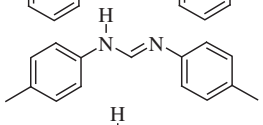
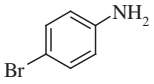
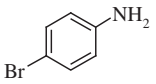
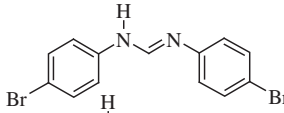
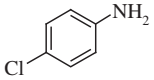
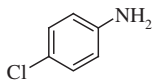
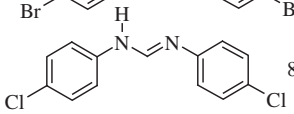
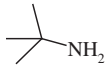
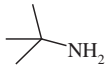
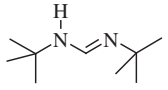
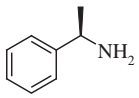
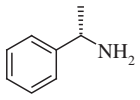
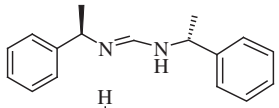
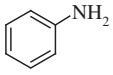
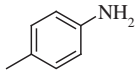
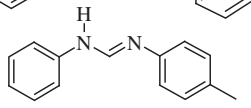
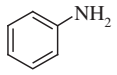
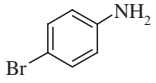
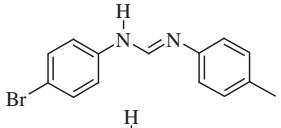
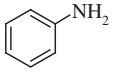
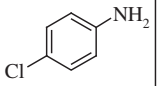
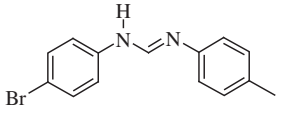
A new perspective seemed to be needed for the efficient workup. Therefore the use of fluorinated solvent seemed to open interesting perspectives for the efficient preparation of these compounds, hoping to greatly simplifying their isolation. Herein, we report an efficient method for synthesizing formamidines which relies exclusively on hydrogen bond activation of orthoesters.

In a preliminary experiment, aniline (2 mmol) in 1 mL HFIP was allowed to stir at room temperature with trimethylorthoformate. The reaction was remarkably fast (3 h) and, after distilling off the HFIP, the amidine **3a** was isolated in 95% yield. Further experiments revealed that a similar procedure is also applicable for the preparation of a wide range of compounds analogous to adduct **3** (Scheme 2).

This method is equally effective with *p*-bromoaniline and *p*-chloroaniline (Scheme 2, entry **4**) bearing electron withdrawing groups on the aromatic ring. After successfully synthesizing a series of formamidine derivatives in high, to excellent yields, we turned our attention towards the synthesis of unsymmetrical formamidine derivatives via unsymmetrical amidination under similar conditions. Thus, in an experiment, we probed the condensation of aniline (1 mmol), trimethylorthoformate (1 mmol) and *p*-toluidine (1 mmol) in HFIP (Scheme 2, entry **7**) for 3 h at room temperature to afford a clean reaction. We carried out the three component coupling reaction of different amines and trimethylorthoformate in HFIP. In all cases, different amines afforded the desired products in high yields under the same reaction conditions as shown in Scheme 2. It is known from the



1 2 3a-i

Entry	Amine 1	Amine 2	Product (%)
1			 95% **3a**
2			 90% **3b**
3			 90% **3c**
4			 80% **3d**
5			 90% **3e**
6			 90% **3f**
7			 90% **3g**
8			 90% **3h**
9			 90% **3i**

Scheme 2. Preparation of formamidine in HFIP.

literature that formamidines with an aliphatic residue, compared to aryl formamidines have a reduced stability and are quickly decomposed to the corresponding amines when exposed to e.g., silica gel [43]. We have also used our method for the synthesis of aliphatic formamidines. Our approach is well suited to prepare aliphatic formamidines in high purity (Scheme 2, entries **3**, **4**). The notable advantages of this method are the operational simplicity, direct use of amines and inexpensive, reusable and non-toxic HFIP medium which render this method an important alternative to previously reported methods.

3. Conclusions

In summary, we have described an efficient methodology for the synthesis of benzimidazole and formamidine derivatives using various electronically and structurally divergent amines in good to excellent isolated yields. In contrast to the existing methods using potentially hazardous catalysts/additives, this new method offers the following competitive advantages: (i) avoiding the use of any base, metal or Lewis acid catalyst, (ii) short reaction times, (iii) ease of product isolation/purification by non-aqueous work-up, (iv) high chemoselectivity, (v) no side reaction, and (vi) low costs and simplicity in process and handling. The recovered HFIP can be reused. Further studies and efforts to extend the scope of this method for other useful reactions are currently underway.

4. Experimental

4.1. General procedure

To a solution containing trimethyl orthoformate (1 mmol), in HFIP (1 mL) was added the amine (2 mmol) or *O*-phenylenediamine (1 mmol) and the mixture was vigorously stirred at r.t. for 2–3 h. The products were isolated after selective evaporation of the HFIP and were purified by a simple silica gel column chromatography eluted by an EtOAc and hexane (4:1) mixture, to afford the corresponding pure disubstituted formamidine or respectively the benzimidazole in very good yields. The physical data (mp, NMR, IR) of *these* known compounds were found to be identical with those reported in the literature. The spectral data for selected products:

1H-Benzimidazole (**1a**): Pale yellow solid, mp 170–171 °C (lit. [14d] 170–172 °C); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.10–7.32 (m, 2H),

7.44–7.66 (m, 2H), 8.11 (s, 1H), 10.75 (br s, NH); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 115.3, 121.3, 137.1, 140.5.

2-Methyl-1H-benzimidazole (**1c**): Pale yellow solid, mp 176–177 °C (lit. [14d] 175–176 °C); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.48 (s, 3H), 7.08–7.10 (m, 2H), 7.44–7.45(m, 2H), 12.2 (br s, NH); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 14.5, 114.2, 121.0, 139.1, 151.2.

2,5-Dimethyl-1H-benzimidazole (**1f**): Pale yellow solid, mp 201–202 °C (lit. [14a] 202–203 °C); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.31 (s, 3H), 2.49 (s, 3H), 7.02 (d, J = 8.0 Hz, 1H), 7.31 (s, 1H), 7.42 (d, J = 8.0 Hz, 1H), 10.76 (br s, NH); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 14.1, 19.5, 114.3, 114.6, 123.6, 131.97, 137.3, 138.7, 155.7.

5-Chloro-2-methyl-1H-benzimidazole (**1k**): Pale yellow solid, mp 136–138 °C (lit. [14a,b] 137–140 °C); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.41 (s, 3H), 7.18 (d, J = 8.8 Hz, 1H), 7.43 (d, J = 8.8 Hz, 1H), 7.51 (s, 1H), 11.20 (br s, NH); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 15.1, 114.69, 115.48, 122.94, 128.04, 137.27, 139.38, 156.90.

N,N′-Diphenyl-formamidine (**3a**): White solid, mp 137–139 °C (lit. [33a,b] 139–140 °C); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.90–7.35 (m, 10H), 8.21(s, 1H), 9.22 (br s, NH); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 119.1, 129.3, 132.6, 143.0, 149.5.

N,N′-Di-p-tolyl-formamidine (**3b**): ^{1}H NMR ($CDCl_3$, 500 MHz): white solid, mp 140–142 °C (lit. [33a] 141–143 °C); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.35(s, 6H), 6.95 (d, J = 8.1 Hz, 4H), 7.12 (d, J = 8.1 Hz, 4H), 8.19 (s, 1H), 9.32 (br s, NH); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 20.7, 119.0, 129.8, 132.6, 143.0, 149.5.

N,N′-Bis-(4-bromo-phenyl)-formamidine (**3c**): White solid, mp 169–170 °C (lit. [33a,b] 170–172 °C); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.89 (d, J = 5.95 Hz, 4H), 7.12(d, J = 5.95 Hz, 4H), 8.09 (s, 1H), 9.52 (br s, NH); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 116.4, 120.7, 132.3, 143.9, 148.8.

N,N′-Bis-(1-phenyl-ethyl)-formamidine (**3f**): Viscous colourless oil [43]; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.55 (d, J = 6.85 Hz, 6H), 4.31–4.36 (m, 2H), 4.47 (q, J = 6.85 Hz, 2H), 7.25–7.41 (m, 11H), 9.89 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 22.7, 57.2, 126.0, 126.1, 128.1, 129.1, 141.8.

N-Phenyl-N′-p-tolyl-formamidine (**3g**): White solid, mp 104–106 °C (lit. [33b] 105–106 °C); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.36 (s, 3H), 6.92–7.35 (m, 9H), 8.24 (s, 1H), 9.12 (br s, NH); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 20.8, 119.1, 123.3, 129.2, 129.4, 129.7, 132.8, 142.7, 145.3, 149.8.

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References

[1] N. Dubrovina, A. Boener, Synthesis 19 (2007) 2925–2943;
J.P. Bégué, D. Bonnet-Delpon, B. Crousse, Synlett (2004) 18–29.
[2] M. Westermaier, H. Mayr, Org. Lett. 8 (2006) 4791–4794.
[3] M.O. Ratnikov, V.V. Tumanov, W.A. Smit, Angew. Chem. Int. Ed. 47 (2008) 9739–9742.
[4] (a) A. Heydari, S. Khaksar, M. Tajbakhsh, Synthesis 19 (2008) 3126–3130;
(b) A. Heydari, S. Khaksar, M. Tajbakhsh, Tetrahedron Lett. 50 (2009) 77–80;
(c) A. Heydari, S. Khaksar, M. Tajbakhsh, H.R. Bijanzadeh, J. Fluorine Chem. 130 (2009) 609–614;
(d) A. Heydari, S. Khaksar, M. Tajbakhsh, H.R. Bijanzadeh, J. Fluorine Chem. 131 (2010) 106–110.
[5] D.A. Horton, G.T. Bourne, M.L. Sinythe, Chem. Rev. 103 (2003) 893–930.
[6] M. Alamgir, St.C.D. Black, N. Kumar, Top. Heterocycl. Chem. 9 (2007) 87–118.
[7] (a) A.R. Porcari, R.V. Devivar, L.S. Kucera, J.C. Drach, L.B. Townsend, J. Med. Chem. 41 (1998) 1252–1262;
(b) T. Rath, M.L. Morningstar, P.L. Boyer, S.M. Hughes, R.W. Buckheitjr, C.J. Michejda, J. Med. Chem. 40 (1997) 4199–4207.
[8] M.T. Migawa, J.L. Girardet, J.A. Walker, G.W. Koszalka, S.D. Chamberlain, J.C. Drach, L.B. Townsend, J. Med. Chem. 41 (1998) 1242–1251.
[9] I. Tamm, Science 126 (1957) 1235–1236.
[10] J. Mann, A. Baron, Y. Opoku-Boahen, E. Johansson, G. Parkinson, L.R. Kelland, S. Neidle, J. Med. Chem. 44 (2001) 138–144.
[11] A. Figge, H.J. Altenbach, D.J. Brauer, P. Tielmann, Tetrahedron: Asymmetry 13 (2002) 137–144.
[12] (a) D.W. Hein, R.S. Alheim, J.J. Leavitt, J. Am. Chem. Soc. 79 (1957) 427–429;
(b) W.O. Pool, H.J. Harwood, A.W. Ralston, J. Am. Chem. Soc. 59 (1937) 178–179;
(c) M. Raban, H. Chang, L. Craine, E. Hortelano, J. Org. Chem. 50 (1985) 2205–2210;
(d) K. Bougrin, M. Soufiaoui, Tetrahedron Lett. 36 (1995) 3683–3686.
[13] D.W. Hein, R.J. Alheim, J.J. Leavitt, J. Am. Chem. Soc. 79 (1957) 427–429.
[14] (a) Z.H. Zhang, L. Yin, Y.M. Wang, Catal. Commun. 8 (2007) 1126–1131;
(b) M.M. Heravi, N. Montazeri, M. Rahmizadeh, M. Bakavoli, M.J. Ghassemzadeh, J. Chem. Res. (S) (2000) 584–585;
(c) D. Villemin, M. Hammadi, B. Martin, Synth. Commun. 26 (1996) 2895–2898;
(d) I.M. Baltork, M. Moghadama, S. Tangestaninejad, V. Mirkhania, M.A. Zolfigol, S.F. Hojatia, J. Iran. Chem. Soc. 5 (2008) 65–70.
[15] (a) A. Ben Alloum, K. Bougrin, M. Soufiaoui, Tetrahedron Lett. 44 (2003) 5935–5937;
(b) P. Gogi, D. Konwar, Tetrahedron Lett. 47 (2006) 79–82;
(c) T. Itoh, K. Nagata, H. Ishikawa, A. Ohsawa, Heterocycles 62 (2004) 197–201;
(d) R. Trivedi, S.K. De, R.A. Gibbs, J. Mol. Catal. A 245 (2006) 8–11.
[16] (a) R.N. Nadaf, S.A. Siddiqui, T. Daniel, R.J. Lahoti, K.V. Srinivasan, J. Mol. Catal. A 214 (2004) 155–160;
(b) M.M. Heravi, M. Tajbakhsh, A.N. Ahmadi, B. Mohajerani, Monatsh. Chem. 137 (2006) 175–179.
[17] H. Wang, R.E. Partch, Y. Li, J. Org. Chem. 62 (1997) 5222–5225.
[18] J.T. Gupton, K.F. Gorreia, B.S. Foster, Synth. Commun. 16 (1986) 365–368.
[19] D.S. VanVliet, P. Gillespie, J.J. Scicinski, Tetrahedron Lett. 46 (2005) 6741–6743.
[20] K. Ziegler-Skylakakis, S. Nill, J.F. Pan, U. Andrae, Environ. Mol. Mutagen. 31 (1998) 362–373.
[21] D.D. Diaz, M.G. Finn, Chem. Eur. J. 10 (2004) 303–309.
[22] T. Goto, H. Sakashita, K. Murakami, M. Sugiura, T. Kondo, C. Fukaya, Chem. Pharm. Bull. 45 (1997) 305–311.
[23] J.W. Liebeschuetz, S.D. Jones, P.J. Morgan, C.W. Marray, A.D. Rimmer, J.M.E. Roscoe, B. Waszkowycz, P.M. Welsch, W.A. Wylie, S.C. Young, H. Martin, J. Mahler, L. Brady, K. Wilkinson, J. Med. Chem. 45 (2002) 1221–1232.
[24] J.L. Collins, B.G. Shearer, J.A. Oplinger, S. Lee, E.P. Garvey, M. Salter, C. Dufry, T.C. Burnette, E.S. Furtine, J. Med. Chem. 41 (1998) 2858–2871.
[25] G.D. Baxter, S.C. Barker, Insect Biochem. Mol. Biol. 29 (1999) 461–467.
[26] S.K. Sridhar, A. Ramesh, Biol. Pharm. Bull. 24 (2001) 1149–1152.
[27] P.J. Dunn, in: A.R. Katritzky, R.J. Taylor (Eds.), Comprehensive Organic Functional Group Transformations II, vol. 5, Elsevier, Oxford, 2005, pp. 655–698;
M. Yokoyama, Y. Menjo, H. Wei, H. Togo, Bull. Chem. Soc. Jpn. 68 (1995) 2735–2738.
[28] D. Toste, J. McNulty, I.W.J. Still, Synth. Commun. 24 (1994) 1617–1624.
[29] S.J. Benkovic, T.H. Barrows, P.R. Farina, J. Am. Chem. Soc. 95 (1973) 8414–8420.
[30] A. Monge, J.A. Palop, M. Gonzalez, F.J. Martinez Crespo, A.L. Decerain, Y. Sainz, S. Narro, A.J. Barker, E. Hamilton, J. Heterocycl. Chem. 32 (1995) 1213–1216.
[31] M.A. Matulenko, A.I. Meyers, J. Org. Chem. 61 (1996) 573–580.
[32] P.S. Furth, M.S. Reitman, R. Gentles, A.F. Cook, Tetrahedron Lett. 38 (1997) 6643–6646.
[33] (a) R.M. Roberts, J. Am. Chem. Soc. 71 (1949) 3848–3849;
(b) R.M. Roberts, J. Am. Chem. Soc. 72 (1950) 3603–3605;
(c) R.M. Roberts, R.H. DeWolfe, J. Am. Chem. Soc. 76 (1954) 2411–2414;
(d) R.M. Roberts, P.J. Vogt, J. Am. Chem. Soc. 78 (1956) 4778–4780.
[34] J. Wang, J.F. Xu, T. Cai, Q. Shen, Org. Lett. 10 (2008) 445–448, and references cited therein.
[35] R. Roger, D.G. Neilson, in: S. Patay (Ed.), The Chemistry of Imidates, Wiley, New York, 1960, p. 179.
[36] A. MacCluskey, P.A. Keller, J. Morgan, J. Garner, Org. Biomol. Chem. 1 (2003) 3353–3361.
[37] N. Kuhnert, I. Clemens, R. Walsh, Org. Biomol. Chem. 3 (2005) 1694–1701.
[38] S. Scherbakow, J.C. Namyslo, M. Gjikaj, A. Schmidt, Synlett (2009) 1964–1968.
[39] E.B. Pederson, D. Carlsen, Chem. Scr. 23 (1984) 123–127.
[40] H. Gielen, C. Alonso-Alija, M. Hendrix, U. Niewoehner, D. Schauss, Tetrahedron Lett. 43 (2002) 419–421.
[41] P.I. Van Vliet, G. Van Koten, K.J. Vrieze, Organomet. Chem. 179 (1979) 89–100.
[42] J.T. Gupton, J.P. Idoux, R. Leonard, Synth. Commun. 13 (1983) 1083–1093.
[43] A. Porcheddu, G. Giacomelli, I. Piredda, J. Comb. Chem. 11 (2009) 126–130.
[44] C.H. Lin, C.H. Tsai, H.C. Chang, Catal. Lett. 104 (2005) 135–140.
[45] L. Cai, Y. Han, S. Rena, L. Huang, Tetrahedron 56 (2000) 8253–8262.