Tetrahedron Letters 52 (2011) 1260–1264

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Guanidine hydrochloride as an organocatalyst for *N*-Boc protection of amino groups

Fatemeh Jahani [a], Mahmood Tajbakhsh [a,*], Hamid Golchoubian [a], Samad Khaksar [b]

[a] Department of Chemistry, University of Mazandaran, Babolsar, Iran
[b] Department of Chemistry, Islamic Azad University, Ayatollah Amoli Branch, Amol, Iran

ARTICLE INFO

Article history:
Received 20 November 2010
Revised 18 December 2010
Accepted 7 January 2011
Available online 14 January 2011

Keywords:
Protection
Organocatalysis
$(Boc)_2O$
Amines
Amino acids

ABSTRACT

A simple and efficient method for the chemoselective *N*-Boc protection of the amine moiety in a variety of compounds is described using di-*tert*-butyl dicarbonate and guanidine hydrochloride as an organocatalyst in ethanol at 35–40 °C. Selective mono-*N*-Boc protection of diamines and chemoselective protection of hydroxylamines without formation of any side products is achieved. Amino acids and peptides are *N*-Boc protected efficiently in excellent yields under convenient reaction conditions.

1. Introduction

The development of mild and selective methods for the protection and deprotection of functional groups continues to be a significant tool in the synthetic chemistry of polyfunctional molecules.[1,2] Protection of the amino group is one of the most fundamental and useful transformations during the synthesis of peptides, amino acids and other natural products. Due to the great stability toward catalytic hydrogenation and resistance toward basic conditions and many other nucleophilic reagents,[3] the *tert*-butoxycarbonyl (Boc) group has been employed extensively to mask the amino function, finding widespread use in both organic[4] and peptide[5] synthesis. Removal of the Boc protecting group is easily performed under various reaction conditions.[1,6] A variety of reagents and methodologies developed over the years, for the preparation of *N*-*tert*-butyl carbamates using di-*tert*-butyl dicarbonate $(Boc)_2O$ have been carried out either in the presence of a base (DMAP,[7] aq NaOH,[8a] NaHMDS,[8b] etc.) or more recently acid catalysts[9–20] and miscellaneous reagents.[21,22] Although well known organocatalysts such as DMAP and *N*-methylimidazole are quite effective, they tend to produce N,N-diacylated amines and isocyanates or heterocycles when *o*-hydroxyanilines or 1,2-diamines are used. In addition, the high toxicity[7e,7f] of and the reagents derived from DMAP restrict its use. Some of the above procedures have certain drawbacks such as formation of side-products, the use of corrosive and moisture-sensitive reagents,[10,23] limited applicabilities,[9] and tedious work-up procedures. Moreover, many of these methods fail when amino acids or peptides are involved.

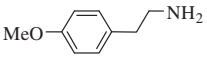
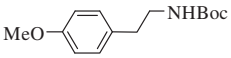
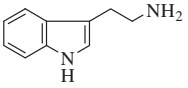
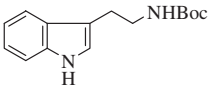
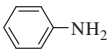
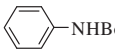
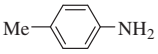
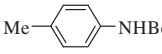
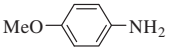
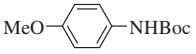
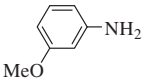
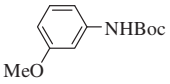
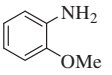
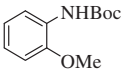
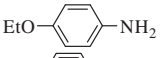
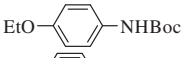
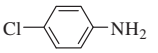
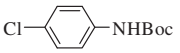
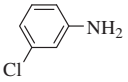
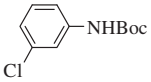
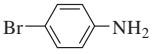
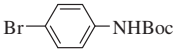
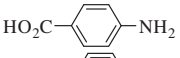
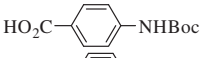
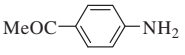
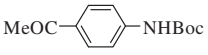
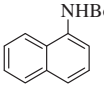
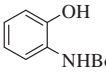
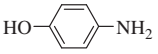
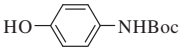
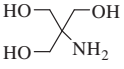
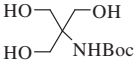
Organocatalysts[24] have been used widely in many reactions as mono and bifunctional catalysts due to economic and environmental considerations. Among the many organocatalysts, hydrogen-bonding compounds such as guanidine derivatives are becoming powerful tools for activation of the carbonyl functionality in organic transformations.[25] In continuation of our interest in the application of organocatalysts in some common acid-catalyzed reactions,[21,26,27] we report a new application of guanidine hydrochloride (Gu·HCl) as an efficient, non-volatile and noncorrosive recyclable catalyst in an alternative method for the metal-free protection of amines, amino acids and peptides with di-*tert*-butyl dicarbonate.

Preliminary experiments were carried out on 4-chloroaniline with $(Boc)_2O$ as a model reaction in various solvents [CH_2Cl_2 (50%), CH_3CN (60%), EtOH (95%), MeOH (95%), H_2O (96%)] in order to find the optimum reaction conditions. It was found that when 4-chloroaniline was treated with 1.2 equiv of $(Boc)_2O$ in the presence of Gu·HCl (15 mol %) in protic solvents at 35–40 °C, after only 55–65 min, *N*-Boc protected 4-chloroaniline was obtained in 95–96% yield (Table 1, entry 14). The lack of generality towards different substrates in water and the toxicity of methanol resulted in utilization of ethanol as the solvent. Moreover, an increase in the amount of the catalyst, from 15 to 25 mol %, did not improve the reaction time and a smaller amount (5 mol %) led to a longer reaction time. Since protection of the α-amino functionality of amino acids is important in the synthesis of peptides and medicinal compounds, and the necessity to preclude polymerization of the amino acid

* Corresponding author. Tel.: +98 112 534 2351; fax: +98 112 534 2350.
E-mail address: Tajbaksh@umz.ac.ir (M. Tajbakhsh).

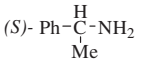
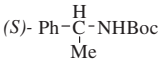
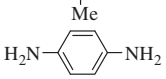
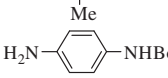
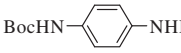
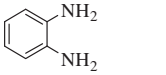
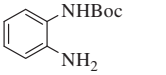
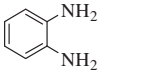
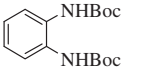
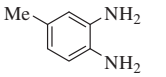
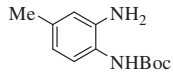
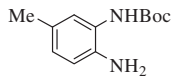
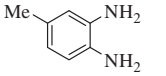
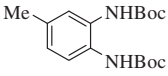
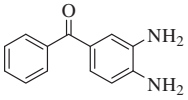
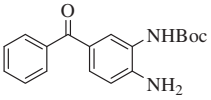
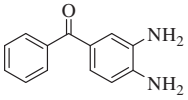
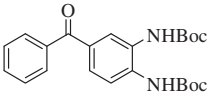
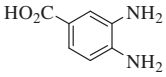
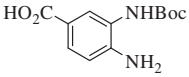
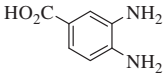
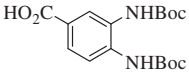
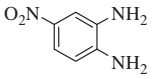
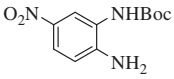
0040-4039/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2011.01.023

Table 1
Gu·HCl-catalyzed protection of amines and diamines.

Entry	Substrate	Product	Time (min)	Yield (%)[a]	Mp (°C) found/reported
1			1	100	Colorless oil/colorless oil[29,30]
2			5	97	Yellow oil/
3			1	100	57–60/56–58[7b,29]
4	$(PhCH_2)_2NH$	$(PhCH_2)_2NBoc$	<1	100	Colorless oil /[12,14]
5	$PhCH_2NH_2$	$PhCH_2NHBoc$	<1	100	54–56/55–57[31,32]
6			<1	100	58–60/
7			3	100	90–92/
8			12	98	132/132[16,29]
9			5	96	84–85/86–87[29,32]
10			5	100	92–94/94–96[14,32]
11			32	97	Yellow oil/[8b]
12			40	95	Colorless oil
13			6	100	110–112
14			65 (55)[b]	95 (96)[b]	102–104/102–103[32]
15			60	95	68–71/69–70[13]
16			60	93	102–103/102[29]
17			2 h	90[c]	181/[7a,33]
18			3 h	87[c]	135–138/137–138[13]
19			65	93	95–97/98–99[32]
20			15	96	142–144/142[29]
21			1	100	146/146[29]
22			5	100	135–137/[15]
23			30	98	Colorless oil
24			2.5 h	95	129–132
25			1	100	46–48/42–45[10]
26			15	95	141–143/144–145[29,34]
27			5.5 h	95	>240
28			1	100[d]	86–88/87–88[32]

(*continued on next page*)

Table 1 (*continued*)

Entry	Substrate	Product	Time (min)	Yield (%)[a]	Mp (°C) found/reported
					
29			5	70	112–114
30			20	98[c]	192–194 dec.
31			3	90	110–113/[12]
32			30	97[c]	105–106/104–106[32]
					
33		+	5	78[e]	105–107
					
34			20	94[c]	158–160
35			17	75	164–166
36			3.5 h	96[f]	136–138
37			40	75	190–192
38			110	93[f]	195–197
39			40	80[c]	190–192

[a] Yield refers to isolated product.
[b] Reaction in H_2O.
[c] Reaction with 2 equiv of $(Boc)_2O$.

once it is activated, the utility of Gu·HCl in the *N*-Boc protection of amino acids and peptides was examined. In traditional methods for *N*-Boc protection of amino acids and peptides an inorganic base or triethylamine is typically used.[28] However, we used the substrates directly without using any base, which is an advantage of this protocol in comparison with those reported in the literature. Treatment of D-phenylalanine with an excess of $(Boc)_2O$ (2.5–3 equiv) in the presence of Gu·HCl (15 mol %) in ethanol at 35–40 °C, afforded an excellent yield of *N*-Boc-D-phenylalanine without any racemization (Table 2, entry 1).

These initial results motivated us to test the generality of the reaction on a variety of structurally diverse amines, amino acids and peptides with $(Boc)_2O$ in the presence of Gu·HCl. Thus, various aliphatic (open chain and cyclic), aromatic, heteroaromatic, heterocyclic amines, diamines, amino acids and peptides were converted in to the corresponding *N*-*tert*-butyl carbamates in good to excellent yields (Tables 1 and 2). The progress of the reactions was monitored by TLC or GC. Competitive side reactions such as the formation of isocyanate, urea, and *N*,*N*-di-Boc derivatives were not detected by TLC and ^1H NMR analysis of the crude products. As can be seen in Table 1, aliphatic amines reacted faster than the aromatic analogues (Table 1, entries 1–7), while aromatic amines required longer reaction times due to their lower nucleophilicity, especially those with electron-withdrawing groups (Table 1, entries 8–19).

The chemoselectivity of Gu·HCl was assessed by performing *N*-Boc protection of amines in bifunctional compounds. Excellent chemoselectivity was observed in the cases of aminoalcohols, aminophenols and hydroxyaminopyridine where the corresponding *N*-Boc protected compounds were formed as sole products without competitive formation of *O*-Boc or oxazolidinone derivatives, even using an excess of $(Boc)_2O$ (Table 1, entries 20–24). It is noteworthy that heteroaromatic amines also underwent Boc-protection in excellent yields (Table 1, entries 24–27). Amines and amino acid esters with stereogenic centers did not undergo racemization or epimerization as confirmed by comparison of the optical rotation values with those reported in the literature (Table 1, entry 28, Table 2, entries 13–15).

Protection of diamines in the presence of Gu·HCl was also studied. It was found that selective mono protection of diamines was achieved using an equivalent of $(Boc)_2O$ (70–90%) and the corresponding *N*,*N*′-di-Boc derivatives were formed as side products

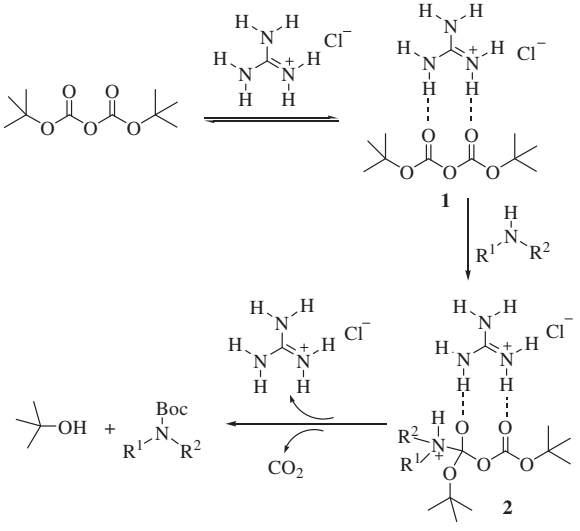
Table 2
Gu·HCl-catalyzed protection of amino acids and peptides

Entry	Product	Time (h)	Yield[a] (%)	Mp (°C)
1	*N*-Boc-D-phenylalanine	6.5	93	Oil[35]
2	*N*-Boc-L-tryptophan	7	97	137–140[36]
3	*N*-Boc-L-proline	30 min	98	137[36]
4	*N*-Boc-glycine	9	96	87–88[36]
5	*N*-Boc-L-leucine	7	90	82–85
6	*N*-Boc-L-valine	7.5	95	77[36,37a]
7	*N*-Boc-glycylglycine	9	96	128–131
8	*N*-Boc-glycylisoleucine	40 min	97	98–100
9	*N*-Boc-glycylvaline	36 min	95	107–108
10	*N*-Boc-glycylphenylalanine	9.5	81	132–135
11	*N*-Boc-alanylalanine	3	93	106–109
12	*N*-Boc-glycylglycylglycine	10	91	125–127
13	*N*-Boc-L-phenylglycine methyl ester	15 min	91[b]	107–110[29,37b]
14	*N*-Boc-L-phenylalanine methyl ester	10 min	97[c]	39–41[29]
15	*N*-Boc-L-leucine methyl ester	22 min	96[d]	Oil

[a] Yield refers to isolated products.
[b] $[\alpha]_D^{27}$ +134.0 (*c* 0.8, $CHCl_3$).
[c] $[\alpha]_D^{27}$ −4.0 (*c* 2, CH_3OH).
[d] $[\alpha]_D^{27}$ −18.3 (neat).

(Table 1, entries 29, 31, 33, 35, 37 and 39). When the amount of $(Boc)_2O$ was increased to 2–3 equiv, rapid formation of di-Boc derivatives occurred (Table 1, entries 30, 32, 34, 36 and 38). Interestingly, in the case of 3,4-diaminonitrobenzene, using 1 equiv of $(Boc)_2O$ afforded only 40% of the mono-*N*-Boc product and introduction of 2 equiv of $(Boc)_2O$ did not result in the di-Boc derivative as expected, but only the mono-*N*-Boc product in 80% yield (Table 1, entry 39).

Finally, we evaluated the effectiveness of this method for the Boc protection of amino acid derivatives. Various amino acids, amino acid esters and peptides were treated with $(Boc)_2O$ using the same approach (Table 2). Amino acids (Table 2, entries 1–6), dipeptides, glycylglycylglycine as a tripeptide (Table 2, entries 7–12) and amino acid esters (Table 2, entries 13–15) were protected efficiently under the reaction conditions without using any additives. An interesting feature of this procedure was that the protection reactions of the amino acids (but not L-proline) and peptides depicted in Table 2 could be monitored visually. This is due to the poor solubility of the starting materials and solubility of the corresponding *N*-Boc derivatives in EtOH. Dissolution in the reaction mixture indicates completion of the reaction.



Scheme 1. The proposed mechanism for *N*-Boc protection of amines.

In order to investigate the mode of catalysis and repeatability of the results with different substrates, further experiments were carried out. Rate acceleration of the reaction was observed when the *N*-Boc protection of *p*-toluidine, 4-chloroaniline, 4-aminobenzoic acid and glycylglycine in the presence and absence of Gu·HCl were compared. In all cases, the reaction rates were enhanced remarkably (see Supplementary data, Table S1).

To explore the recyclability of the catalyst, Gu·HCl was recovered from the *tert*-Butoxycarbonylation of 4-chloroaniline, 4-methoxyaniline and tryptophan by washing the crude products with water and then using it in three successive runs with only a minor loss of the activity (see Supplementary data, Table S2).

According to the above observations and previous reports on the electrophilic activation of carbonyl groups through hydrogen bonding with Gu·HCl,[26,38,39] and Boc activation by protic solvents such as ethanol[32] and water,[29] it is postulated that this reaction could proceed through activation of the $(Boc)_2O$ carbonyl groups by hydrogen bonding with the catalyst to form species **1**. This facilitates subsequent attack of the amino group on the carbonyl carbon to give species **2**, followed by the elimination of CO_2 and *t*-BuOH to afford the carbamate. Hydrogen bonding of the nitrogen atom of guanidine hydrochloride with the hydrogen atom of the amine (nucleophilic activation), possibly accelerates the formation of species **2** (Scheme 1).[38]

To underline the advantages of this method, the *N*-Boc protections of amines using Gu·HCl were faster and gave higher yields than those with the catalysts reported in the literature (see Supplementary data, Table S3). For instance, the reaction of 4-methoxyaniline with $(Boc)_2O$ afforded the product in 94% yield after 6 h in the presence of yttria-zirconia in MeCN,[9] 99% yield after 6 h in *t*-BuOH in the presence of $Zn(ClO_4)_2{\cdot}6H_2O$,[11] 86% yield after 1.5 h in the presence of I_2 under solvent-free conditions,[14] 96% yield after 40 min under solvent and catalyst free conditions[40] and 78% yield after 1.5 h in the presence of β-CD in water,[41] whereas, a quantitative yield was obtained after only 5 min in the presence of Gu·HCl in ethanol.

It is noteworthy that many of the reported methods do not show generality, especially for amino acids and peptides, without using additive.[11,14,28]

In conclusion, we have shown that Gu·HCl can be used as an efficient catalyst for selective and chemoselective *N*-Boc protection of amines, diamines, amino acids and peptides. The catalyst can be recovered and reused in the subsequent runs without losing significant catalytic activity. Simple work-up, very mild reaction conditions, reusability of the catalyst and high yields of products are other advantages of this protocol.

2. General procedure for the preparation of *N*-Boc amines and diamines

The amine or diamine (1 mmol) was added to a stirred solution of Gu·HCl (15 mol %) and $(Boc)_2O$ (1.2–3 mmol) in EtOH (1 mL), at 35–40 °C and stirred for the appropriate amount of time (Table 1). After completion of the reaction (followed by TLC or GC), the EtOH was evaporated and the residue was either washed with H_2O or dissolved in CH_2Cl_2 (or EtOAc) and filtered to separate the catalyst. Evaporation of the organic solvent (if used in the work-up) gave almost pure products. In the cases where excess $(Boc)_2O$ was used, the products were washed with petroleum–ether or hexane to recover the residual $(Boc)_2O$.

3. General procedure for the preparation of *N*-Boc amino acids and peptides

Amino acid or peptide (1 mmol) was added to a solution of Gu·HCl (15 mol %) and $(Boc)_2O$ (2.5–3 mmol) in EtOH (1 mL), at

35–40 °C. The reaction mixture was stirred until a clear solution was obtained. The EtOH was evaporated under vacuum and the residue was washed successively with H_2O (2 mL) and hexane or petroleum ether (2 mL) to afford almost pure *N*-Boc amino acids or *N*-Boc peptides. If necessary, the crude products were recrystallized.

All the products were characterized by mp, ^1H and ^{13}C NMR spectroscopy, microanalysis and by comparison with authentic samples reported in the literature.

3.1. *N*-(*tert*-Butoxycarbonyl)-2-amino-3-hydroxypyridine (Table 1, entry 24)

Off-white solid, yield: 95%; mp: 129–132 °C; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.54 (s, 9H), 7.00 (dd, J = 8, 4.7 Hz, 1H), 7.32 (dd, J = 8, 1.5 Hz, 1H), 7.91 (dd, J = 4.7, 1.5 Hz, 1H), 9.31 (s, 1H, OH), 9.96 (br s, 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.2 (CH_3), 83.1 (C), 121.2 (CH), 127.8 (CH), 138.8 (CH), 140.3 (C), 143.8 (C), 156.1 (C=O); Anal. Calcd for $C_{10}H_{14}N_2O_3$: C, 57.13; H, 6.71; N, 13.32. Found: C, 56.33; H, 6.64; N, 13.20.

3.2. *N*-Boc-L-proline (Table 2, entry 3)

White solid, yield: 98%; mp: 137 °C; ^1H NMR (300 MHz, $CDCl_3$): (1:0.9 rotamer ratio, the asterisk denotes minor rotamer peaks), δ = 1.40 (s, 9H), 1.45* (s, 9H), 1.85–2.00 (m, 4H), 2.04–2.25 (m, 4H), 3.31–3.55 (m, 4H), 4.22 (m, 1H), 4.33* (m, 1H), 11.31 (br s, 2H, CO_2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.6 (CH_2), 24.3* (CH_2), 28.2 (CH_3), 28.4* (CH_3), 29.0* (CH_2), 30.8 (CH_2), 46.3 (CH_2), 46.9* (CH_2), 58.9 (CH), 80.3 (C), 81.0* (C), 153.9 (C=O), 155.9* (C=O), 176.2* (CO_2H), 178.9 (CO_2H).

Acknowledgement

The authors are thankful to the University of Mazandaran research council for partial financial support.

Supplementary data

Experimental procedures, analytical and spectral characterization details, comparison tables, copies of ^1H and ^{13}C NMR spectra of compounds in Table 1 (entries 2, 3, 6, 7, 10, 12–14, 16, 17, 23, 24, 27, 30 and 33–39) and Table 2 (entries 1–4, 7–12 and 15) are provided. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.01.023.

References and notes

1. Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 3rd ed.; John Wiley and Sons: New York, 1999.
2. Kocienski, P. J. *Protecting Groups*; George Thieme: Stuttgart, New York, 2004.
3. (a)Wuensch, E., Ed., 4th ed.Houben-Weyl, Methods of Organic Chemistry; Muller, E., Bayer, O., Meerwin, H., Ziegler, K., Eds.; George Thieme: Stuttgart, New York, 1974; Vol. 15/1, p 46; (b) Xiuo, X. Y.; Ngu, K.; Chao, C.; Petal, D. V. *J. Org. Chem.* **1997**, *62*, 6968.
4. (a) Carpino, L. A.; Parameswaran, K. N.; Kirkley, R. K.; Spiewak, J. W.; Schmitz, E. *J. Org. Chem.* **1970**, *35*, 3291; (b) Almeida, M. L. S.; Grehn, L.; Ragnarsson, U. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1905; (c) Dieter, R. K.; Dieter, J. W.; Alexander, C. W.; Bhinderwala, N. S. *J. Org. Chem.* **1996**, *61*, 2930; (d) Burkhart, F.; Hoffmann, M.; Kessler, H. *Angew. Chem., Int. Ed.* **1997**, *36*, 1191.
5. Kaiser, E. S.; Picart, F.; Kubiak, T.; Tam, J. P.; Merrifield, R. B. *J. Org. Chem.* **1993**, *58*, 5167.
6. (a) Kazzouli, S. E.; Koubachi, J.; Berteina-Raboin, S.; Mouaddib, A.; Guillaumet, G. *Tetrahedron Lett.* **2006**, *47*, 8575; (b) Wang, G.; Li, C.; Li, J.; Jia, X. *Tetrahedron Lett.* **2009**, *50*, 1438; (c) Navath, R. S.; Pabbisetty, K. B.; Hu, L. *Tetrahedron Lett.* **2006**, *47*, 389; (d) Tom, N. J.; Simon, W. M.; Frost, H. N.; Ewing, M. *Tetrahedron Lett.* **2004**, *45*, 905.
7. (a) Darnbrough, S.; Mervic, M.; Condon, S. M.; Burns, C. J. *Synth. Commun.* **2001**, *31*, 3273; (b) Basel, Y.; Hassner, A. *J. Org. Chem.* **2000**, *65*, 6368; (c) Burk, M. J.; Allen, J. G. *J. Org. Chem.* **1997**, *62*, 7054; (d) Grehn, L.; Ragnarsson, U. *Angew. Chem., Int. Ed.* **1985**, *24*, 510; (e)*Registry of Toxic Effects of Chemical Substances 1985–86*; Sweet, D. V., Ed.; US Govt. Printing Office: Washington, DC, 1988. p 3336; (f)*Registry of Toxic Effects of Chemical Substances 1985–86*; Sweet, D. V., Ed.; US Govt. Printing Office: Washington, DC, 1988. p 4049.
8. (a) Lutz, C.; Lutz, V.; Knochel, P. *Tetrahedron* **1998**, *54*, 6385; (b) Kelly, T. A.; McNeil, D. W. *Tetrahedron Lett.* **1994**, *35*, 9003.
9. Panndey, R. K.; Dagade, S. P.; Upadhyay, R. K.; Dongare, M. K.; Kumar, P. *ARKIVOC* **2002**, *vii*, 28.
10. Sharma, G. V. M.; Reddy, J. J.; Lakshmi, P. S.; Krishna, P. R. *Tetrahedron Lett.* **2004**, *45*, 6963.
11. Bartoli, G.; Bosco, M.; Locatelli, M.; Marcantoni, E.; Massaccesi, M.; Melchiorre, P.; Sambri, L. *Synlett* **2004**, 1794.
12. Heydari, A.; Hosseini, S. E. *Adv. Synth. Catal.* **2005**, *347*, 1929.
13. Chankeshwara, S. V.; Chakraborti, A. K. *Tetrahedron Lett.* **2006**, *47*, 1087.
14. Varala, R.; Nuvula, S.; Adapa, S. R. *J. Org. Chem.* **2006**, *71*, 8283.
15. Heydari, A.; Kazem Shiroodi, R.; Hamadi, H.; Esfandyari, M.; Pourayoubi, M. *Tetrahedron Lett.* **2007**, *48*, 5865.
16. Chankeshwara, S. V.; Chakraborti, A. K. *J. Mol. Catal. A: Chem.* **2006**, *253*, 198.
17. Das, B.; Verkateswarlu, K.; Krishnaiah, M.; Holla, H. *Tetrahedron Lett.* **2006**, *47*, 7551.
18. Suryakiran, N.; Prabhakar, P.; Srikanth Reddy, T.; Rajesh, K.; Venkateswarlu, Y. *Tetrahedron Lett.* **2006**, *47*, 8039.
19. Upadhyaya, D. J.; Barge, A.; Stefania, R.; Cravotto, G. *Tetrahedron Lett.* **2007**, *48*, 8318.
20. Chankeshwara, S. V.; Chakraborti, A. K. *Synthesis* **2006**, 2784.
21. (a) Khaksar, S.; Heydari, A.; Tajbakhsh, M.; Vahdat, S. M. *Tetrahedron Lett.* **2008**, *49*, 3527; (b) Heydari, A.; Khaksar, S.; Tajbakhsh, M. *Synthesis* **2008**, 3126; (c) Khaksar, S.; Vahdat, S. M.; Tajbakhsh, M.; Jahani, F.; Heydari, A. *Tetrahedron Lett.* **2010**, *51*, 6388.
22. (a) Akbari, J.; Heydari, A.; Ma'mani, L.; Hosseini, S. H. *Compd. Rendus Chim.* **2010**, *13*, 544; (b) Sunitha, S.; Kanjilal, S.; Reddy, P. S.; Prasad, R. B. N. *Tetrahedron Lett.* **2008**, *49*, 2527.
23. Schumacher, J. C. *Perchlorates—Their Properties, Manufacture and Uses. ACS Monograph Series*; Reinhold: NewYork, 1960; (b) Long, J. R. *Chem. Health Saf.* **2002**, *9*, 12.
24. (a) Dalko, P. I.; Moisan, L. *Angew. Chem., Int. Ed.* **2001**, *40*, 3726; (b) List, B. *Tetrahedron* **2002**, *58*, 5573; (c) Duthaler, R. O. *Angew. Chem., Int. Ed.* **2003**, *42*, 975; (d) Schreiner, P. R. *Chem. Soc. Rev.* **2003**, *32*, 289; (e) Pihko, P. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 2062; (f) Connon, S. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 3909; (g) List, B. *Chem. Commun.* **2006**, 819; (h) Enders, D.; Grondal, C.; Hüttl, M. R. M. *Angew. Chem., Int. Ed.* **2007**, *46*, 1570; (i) Connon, S. J. *Org. Biomol. Chem.* **2007**, *5*, 3407.
25. (a) MacMillan, D. W. C. *Nature* **2008**, *455*, 304; (b) Doyle, A. G.; Jacobsen, E. N. *Chem. Rev.* **2007**, *107*, 5713.
26. Heydari, A.; Arefi, A.; Khaksar, S.; Tajbakhsh, M. *Catal. Commun.* **2006**, *7*, 982.
27. (a) Jahani, F.; Zamenian, B.; Khaksar, S.; Tajbakhsh, M. *Synthesis* **2010**, 3315; (b) Heydari, A.; Khaksar, S.; Tajbakhsh, M.; Bijanzadeh, H. R. *J. Fluorine Chem.* **2009**, *130*, 609; (c) Heydari, A.; Khaksar, S.; Tajbakhsh, M. *Tetrahedron Lett.* **2009**, *50*, 77; (d) Vahdat, S. M.; Baharfar, R.; Tajbakhsh, M.; Heydari, A.; Baghbanian, S. M.; Khaksar, S. *Tetrahedron Lett.* **2008**, *49*, 6501.
28. (a) Ponnusamy, E.; Fotadar, U.; Spisni, A.; Fiat, D. *Synthesis* **1986**, 48; (b) Shendage, M. D.; Frohlich, R.; Haufe, G. *Org. Lett.* **2004**, *6*, 3675.
29. Chankeshwara, S. V.; Chakraborti, A. K. *Org. Lett.* **2006**, *8*, 3259.
30. Dieter, R. K.; Li, S. *J. Org. Chem.* **1997**, *62*, 7726.
31. Strazzolini, P.; Melloni, T.; Giumanini, A. G. *Tetrahedron* **2001**, *57*, 9033.
32. Vilaivan, T. *Tetrahedron Lett.* **2006**, *47*, 6739.
33. Norman, M. H.; Rigdon, G. C.; Hall, W. R.; Navas, F., III *J. Med. Chem.* **1996**, *39*, 1172.
34. Venuti, M. C.; Stephenson, R. A.; Alvarez, R.; Bruno, J. J.; Strosberg, A. M. *J. Med. Chem.* **1988**, *31*, 2136.
35. Myers, A. G.; Gleason, J. L.; Yoon, T.; Kung, D. W. *J. Am. Chem. Soc.* **1997**, *119*, 656.
36. Anderson, G. W.; McGregor, A. C. *J. Am. Chem. Soc.* **1957**, *79*, 6180.
37. (a) Thaqi, A.; McCluskey, A.; Scott, J. L. *Tetrahedron Lett.* **2008**, *49*, 6962; (b) Dondoni, A.; Perrone, D.; Semola, T. *Synthesis* **1995**, 181.
38. (a) Tanaka, S.; Nagasawa, K. *Synlett* **2009**, 667; (b) Braddock, D. C.; MacGilp, I. D.; Perry, B. G. *Adv. Synth. Catal.* **2004**, *346*, 1117; (c) Sohtome, Y.; Nagasawa, K. *Synlett* **2010**, 1.
39. Smetana, A. J.; Popov, A. I. *J. Solution Chem.* **1980**, *6*, 183.
40. Jia, X.; Huang, Q.; Li, J.; Li, S.; Yang, Q. *Synlett* **2007**, 806.
41. Reddy, M. S.; Narender, M.; Nageswar, Y. V. D.; Rao, K. R. *Synlett* **2006**, 1110.