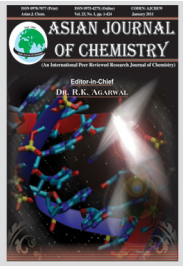
Asian Journal of Chemistry; Vol. 23, No. 9 (2011), 4165-4168

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in



Synthesis of β-Amino Cyclone Catalyzed by Alkaline Al_2O_3

W.F. XU[1], Q. CHEN[2], R.Q. LIU[1], F.B. REN[1], Y.F. ZHOU[1,*] and X.L. LU[1,*]

[1]College of Life Sciences, China Jiliang University, Xiasha, Hangzhou 310018, Zhejiang, P.R. China
[2]Zhejiang Apeloa Medical Technology Co. Ltd., Dongyang 322118, Zhejiang, P.R. China

*Corresponding authors: Tel: +86 571 86835702; E-mail: cjluyh@163.com; imxuweifeng@163.com

(*Received*: 31 December 2010; *Accepted*: 25 May 2011) AJC-9990

A new method for the synthesis of β-amino cyclone with amines and cyclonene, which was efficiently carried out under solvent free conditions in a short time at room temperature using the catalyst of alkaline Al_2O_3 with high yield. The reusability of the catalyst has been successfully examined without noticeable loss of its catalytic activity.

Key Words: Alkaline Al_2O_3, Cyclohexenone, Cyclonene, Cyclopentenone, Solvent-free.

INTRODUCTION

As the β-amino cycloketone has been recognized as not only a key structure of biologically important natural products including β-lactams but also a versatile nitrogen-containing intermediate such as amino alcohols, diamines and β-amino acid derivatives. Owing to their wide range of biological activities and pharmacological properties, the synthesis of β-amino cycloketone compounds, particularly β-amino cyclopentanone and β-amino cyclohexanone, has become a field of increasing interest in organic synthesis during the past few decades. The approach based on conjugate addition of amines to cyclonene is one of the simplest and most effective methods for preparing β-amino cyclone compounds. In recent years, a number of catalysts such as [Bmim]PF_6[1], TBAB[2], $HClO_4$-SiO_2[3], SiO_2@Cu-Core-Shell-Nanoparticles[4], *n*-Bu_4NBr-KOH[5], TEAA[7], [DUB][Ac][8], [DUB][Lac][9], nano-Cu[10], $Bi(NO_3)_3$[11], $Cu(OTf)_2$[12], $FeCl_3$-Me_3SiCl[13], (*n*-Bu)$_3$P-Me_3S iCl[14], $Cu(acac)_2$[15], [Bmim]OH[16], $[HP(HNCH_2CH_2)_3N]NO_3$[17], PAPh[18], (IPr)Cu(NHPh)(I)[19], PANI-In[20] have been developed for this reaction. Furthermore, transition metal salt catalysts were reported over the past few years, for instance, $PtCl_4$[21], $ZrOCl_2$[23], $Hf(OTf)_4$[24], $VO(OTf)_2$[25], Pd/Rh[22], $ZrCl_4$[26], ZrO_2/SO_4^{2-} [27], $VO(OAc)_2$[28], $Zr(DS)_4$[29], $Co(OAc)_2$[30]. However, most of the methods have the drawbacks of using expensive and/or toxic catalysts, harsh reaction conditions[31], low yields[6] or long reaction time limited their application in organic synthesis[32]. As more and more attention is paid to introduction of cleaner technologies both in industry and academia, preparation and application of recyclable catalysts have become a high priority. The practical and economic methods in large-scale operations require the development of efficient and recyclable catalytic systems. Hence, the requirement of developing a new conjugate addition of aromatic amines to cyclonene and mild reaction condition remains. As alkaline Al_2O_3 was widely used in organic synthesis[33]. In this paper, we describe the use of recyclable alkaline Al_2O_3 as an efficient and versatile catalyst for the conjugate addition of aromatic amines to cyclonene. The reaction was carried out under mild condition with high yield in the absence of solvent and alkaline Al_2O_3 could be readily recycled at least five times without obvious deactivation.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were recorded on a Bruker ACF 400. Column chromatography was performed on silica gel. Alkaline Al_2O_3 and other chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd.

General procedure: A mixture of aromatic amine (10 mmol), cyclonene (12 mmol) and alkaline Al_2O_3 (1 g) was stirred at room temperature for 2 h (monitored by TLC). Then, the solid mixture was washed with ethyl acetate (10 mL) and the crude product was obtained after removing off the ethyl acetate from washing solution. Further purification was carried out by short column chromatography on silica gel(ethyl acetate: *n*-hexane = 1:6). The recovered alkaline Al_2O_3 could be reused.

RESULTS AND DISCUSSION

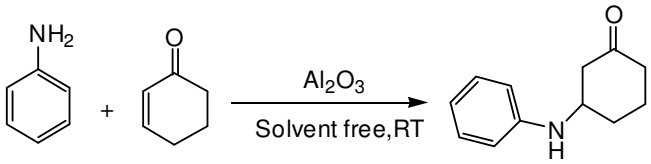
In order to optimize the reaction conditions, initially, the condensation of cyclohexenone and phenylamine was studied as a model reaction at room temperature (Table-1 and

TABLE-1
OPTIMIZATION OF REACTION OF CYCLOHEXENONE TO PHENYLAMINE AT ROOM TEMPERATURE[a]

Entry	Catalyst (g)	Time (h)[c]	Yield (%)[d]
1[b]	0	26.0	78
2	0.50	9.0	97
3	0.75	4.5	98
4	1.00	2.0	98
5	1.25	2.0	98
6	1.50	2.0	98
7	1.75	2.0	98

[a]All reactions were run at room temperature using cyclohexenone (12 mmol), phenylamine (10 mmol) without solvent. [b]No addition of alkaline Al_2O_3. [c]The time of the reaction was monitored by TLC (AcOEt: *n*-hexane = 1:4). [d]Isolated yields after column chromatography(AcOEt: *n*-hexane =1:6).

Scheme-I)and the reaction finished in 2 h with the yield of 98 %. In the absence of the catalyst, the reaction finished after 26 h and had the isolated yields of 78 %. Optimization for using amount of the alkaline Al_2O_3 revealed that the best yield was obtained when 1 g alkaline Al_2O_3 was used under the experimental scale.



Scheme-I: Reaction of cyclohexenone to phenylamine at room temperature

In order to show the general applicability of present method, the addition of several aromatic amines to cyclopentenone and cyclohexenone were catalyzed by alkaline Al_2O_3 in proper time and with good to excellent yields (Table-2). It is notable that no by-products were produced resulting from the undesirable 1,2-addition or *bis*-addition side reactions which are usually observed under classical conditions.

The reaction of cyclic amine N-methylmorpholine with cyclohexenone and cyclopentenone gave 99 and 97 % yield, respectively, in 1.5 h (Table-2, entries 6 and 10). Sterically hindered amine, for example phenylamine (Table-2, entry 1 and 7) with cyclohexenone and cyclopentenone offered 1,4-addtion products in 98 and 95 % yield in 2 h.

Recycling of the catalyst is important for the large-scale operation and industrial point of view. To check the possibility of the catalyst recycling, addition of cyclohexenone with phenylamine at room temperature in alkaline Al_2O_3 was studied. After the completion of the reaction, EtOAc was added to reaction mixture. Then, the organic phase was separated and remainder was filtered. The isolated solid phase (alkaline Al_2O_3) was washed for several times and dried under reduced pressure then reused for five runs without any noticeable drop in the yield and catalytic activity(Table-3).

Analytical data of the products

3-(Phenylamino)cyclohexanone: (Table-2, entry 1) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.191-7.160 (m, 2H), 6.736-6.706 (m, 1H), 6.601-6.585 (d, *J* = 6.4, 2H), 3.816-3.765 (m, 1H), 2.857-2.815 (m, 1H), 2.440-2.365 (m, 1H), 2.353-2.262 (m, 2H), 2.199-2.168 (m, 1H), 2.090-2.027 (m, 1H), 1.796-1.695 (m, 2H), 1.689-1.586 (m, 1H); ^{13}C NMR (400 MHz, $CDCl_3$): δ = 209.55, 146.24, 129.39, 117.87, 113.29, 52.27, 48.53, 51.12, 31.04, 22.11; ESI-MS: m/z 189.96 $[M + 1]^+$. NMR data were identical with those described in the literature[32b].

3-(*o*-Toluidino)cyclohexanone: (Table-2, entry 2) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.275 (s, 1H), 7.153-7.079 (m, 1H), 6.712-6.681 (m, 1H), 6.637-6.621 (d, *J* = 6.4, 1H), 3.883-3.848 (m, 1H), 2.907-2.864 (m, 1H), 2.464-2.350 (m, 1H), 2.347-2.320 (m, 2H), 2.235-2.189 (m, 1H), 2, 146 (s, 3H), 2.101-2.061 (m, 1H), 1.815-1.765 (m, 1H); ^{13}CNMR (400 MHz,$CDCl_3$): δ = 209.57, 144.18, 130.41, 127.16, 122.14, 117.40, 110.37, 52.07, 48.65, 41.16, 31.12, 22.19, 17.48; ESI-MS: m/z 203.88 $[M + 1]^+$. NMR data were identical with those described in the literature[9].

3-(*p*-Toluidino)cyclohexanone: (Table-2, entry 3) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.995-6.978 (d, *J* = 6.8, 2H), 6.531-6.514 (m, 2H), 3.767-3.731 (m, 1H), 2.841-2.802 (m, 1H), 2.422-2.244 (m, 4H), 2.242-2.233 (d, *J* = 3.6, 3H), 2.193-2.153 (m, 1H), 2.067-2.022 (m, 1H), 1.759-1.676 (m, 2H); ^{13}C NMR (400 MHz, CDCl3): δ = 209.73, 144.00, 129.91, 127.19, 113.65, 52.68, 48.64, 41.18, 31.12, 22.16, 20.39; ESI-MS: m/z 204.11 $[M + 1]^+$. NMR data were identical with those described in the literature[9].

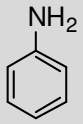
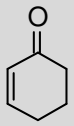
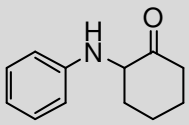
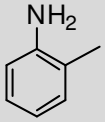
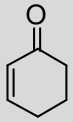
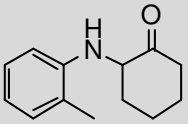
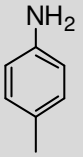
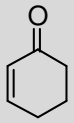
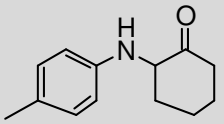
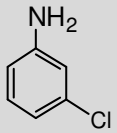
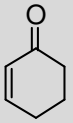
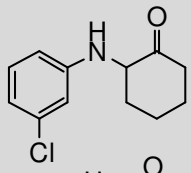
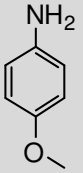
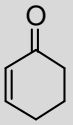
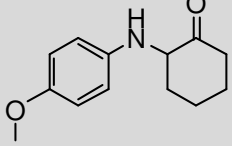
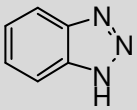
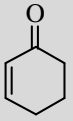
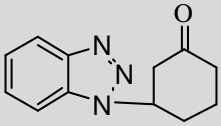
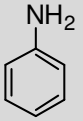
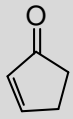
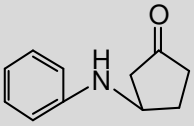
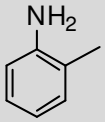
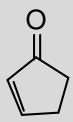
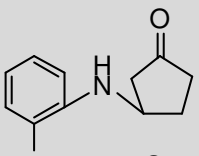
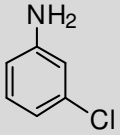
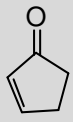
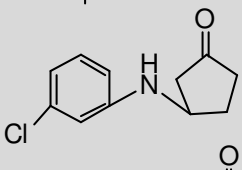
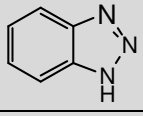
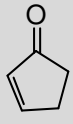
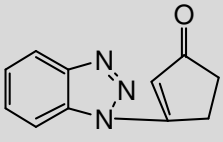
3-(3-Chlorophenylamino)cyclohexanone: (Table-2, entry 4) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.096-7.064 (s, 1H), 6.694-6.676 (m, 1H), 6.575-6.544 (m, 1H), 6.471-6.449 (m, 1H), 3.663-3.545 (m, 1H), 2.841-2.804 (m, 1H), 2.454-2.409(m, 1H), 2.406-2.211 (m, 2H), 2.201-2.161 (m, 1H), 2.075-2.037 (m, 1H), 1.799-1.697 (m, 1H). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 209.26, 147.48, 135.12, 130.38, 117.63, 112.82, 111.53, 52.07, 48.25, 41.07, 30.83, 22.03; ESI-MS: m/z 223.94 $[M + 1]^+$. NMR data were identical with those described in the literature[9].

3-(4-Methoxyphenylamino)cyclohexanone: (Table-2, entry 5) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.780-6.758 (d, *J* = 8.8, 2H), 6.580-6.558 (d, *J* = 8.8, 2H), 3.732 (s, 3H), 3.687-3.668 (m, 1H), 3.177 (s, 1H), 2.813-2.768 (m, 1H), 2.406-2.221 (m, 3H), 2.167-2.133 (m, 1H), 2.060-2.006 (m, 1H), 1.742-1.631 (m, 1H). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 209.76, 152.43, 140.41, 115.10, 114.95, 55.71, 53.33,4 8.58, 41.10, 31.12, 22.09; ESI-MS: m/z 219.96 $[M + 1]^+$. NMR data were identical with those described in the literature[29].

3-(3a*H*-Benzo[d][1,2,3]triazol-1(7a*H*)-ylamino)-cyclohexanone: (Table-2, entry 6) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.100-8.083 (d, *J* = 6.8, 1H), 7.543-7.497 (m, 2H), 7.416-7.383 (m, 1H), 5.069-5.009 (m, 1H), 3.335-3.284 (m, 1H), 2.988-2.949 (m, 1H), 2.574-2.512 (m, 2H), 2.497-2.490 (m, 1H), 2.430-2.395 (m, 1H), 2.229-2.183 (m, 1H), 1.896-1.820 (m, 1H); ^{13}C NMR(400 MHz, $CDCl_3$): δ = 205.79, 145.93, 132.10, 127.45, 124.17, 120.09, 109.20, 56.78, 46.92, 40.52, 30.89, 21.76; ESI-MS: m/z 215.94 $[M - 1]^+$. NMR data were identical with those described in the literature[34].

3-(Phenylamino)cyclopentanone: (Table-2, entry 7) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.261-7.133 (m, 2H), 6.773-6.736 (m, 1H), 6.697-6.677 (m, 1H), 6.636-6.616 (m, 1H), 4, 146-4.0 87 (m, 1H), 2.739-2.677 (m, 2H), 2.373-2.350 (m, 2H), 2.311-2.200 (m, 2H), 1.989-1.965 (m, 1H); ^{13}C NMR

TABLE-2
CONJUGATIVE ADDITION OF AROMATIC AMINE TO CYCLOPENTENONE AND CYCLOHEXENONE AT ROOM TEMPERATURE[a]

Entry	Amine	Cyclonene	Product	Time(h)[b]	Isolated Yield%[c]
1				2	98
2				2	95
3				2	95
4				2	96
5				2	98
6				1.5	99
7				2	95
8				2	95
9				2	95
10				1.5	97

[a]All reactions were run at room temperature using cyclohexenone (12 mmol), phenylamine (10 mmol) without solvent. [b]The time of the reaction was monitored by TLC(AcOEt: *n*-hexane=1:4). [c]Isolated yields after column chromatography(AcOEt: *n*-hexane =1:6).

(400 MHz, $CDCl_3$): δ = 217.16, 165.03, 146.92, 134.55, 118.05, 115.14, 113.35, 51.16, 46.06, 36.61, 29.00; ESI-MS: m/z 175.93 $[M + 1]^+$. NMR data were identical with those described in the literature[16].

3-(*o*-Toluidino)cyclopentanone: (Table-2, entry 8) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.162-7.124 (m, 1H), 7.088-7.069 (m, 1H), 6.730-6.693 (m, 1H), 6.648-6.628 (m, 1H), 4.194-4.136 (m, 1H), 2.779-2.171 (m, 1H), 2.511-2.436 (m, 2H), 2.417-2.370 (m, 1H), 2.331-2.186 (m, 1H), 2.127 (s, 3H), 2.058-2.014 (m, 1H), 1.303-1.255 (m, 1H); ^{13}C NMR (400 MHz, $CDCl_3$): δ = 217.08, 144.81, 130.44, 127.16, 122.51, 118.60, 110.49, 51.02, 46.29, 36.57, 29.87, 17.55; ESI-MS:

TABLE-3
RECYCLING USE THE CATALYST OF ALKALINE Al_2O_3 FOR FIVE TIMES

Times	Catalyst (g)	Time (h)[c]	Yield (%)[d]
1[a]	1	2	98
2[a]	1	2	98
3[b]	0.5	2	98
4[b]	0.5	2	95
5[b]	0.5	2	95

[a]The reactions were run at room temperature using cyclohexenone(12mmol), phenylamine (10mmol) , reused alkaline $Al_2O_3$1g without solvent. [b]The reactions were run at room temperature using cyclohexenone (6 mmol), phenylamine (5 mmol), reused alkaline Al_2O_3 0.5 g without solvent. [c]The time of the reaction was monitored by TLC (AcOEt: *n*-hexane = 1:4). [d]Yield refers to HPLC (*n*-hexane: isopropanol = 1:8).

m/z 189.98 $[M + 1]^+$. NMR data were identical with those described in the literature[9].

3-(3-Chlorophenylamino)cyclopentanone: (Table-2, entry 9) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.114-7.074 (m, 1H), 6.725-6.705 (m, 1H), 6.620-6.592 (m, 1H), 6.496-6.470 (m, 1H), 4, 104-4.074 (m, 1H), 2.743-2.681 (m, 1H), 2.467-2.358 (m, 3H), 2.324-2.263 (m, 1H), 2, 191- 2.130 (m, 1H), 1.998-1.965 (m, 1H); ^{13}C NMR (400 MHz, $CDCl_3$): δ = 216.49, 148.00, 135.14, 130.36, 117.89, 112.90, 111.65, 51.03, 45.82, 36.51, 29.64; ESI-MS: m/z 209.99 $[M + 1]^+$.

3-(3a*H*-Benzo[d][1,2,3]triazol-1(7a*H*)-ylamino)-cyclopentanone: (Table-2, entry 10) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.114-8.093 (d, *J* = 8.4, 1H), 7.575-7.396 (m, 2H), 7.264 (s, 1H), 5.498-5.436 (m, 1H), 3.148- 3.087 (m, 1H), 2.974-2.891 (m, 1H), 2.779-2.681 (m, 4H), 2.503-2.443 (m, 1H); ^{13}C NMR (400 MHz, $CDCl_3$): δ = 213.94, 146.23, 132.52, 127.59, 124.29, 120.27, 109.11, 55.76, 44.03, 36.64, 29.63; ESI-MS: m/z 203.95 $[M + 1]^+$. NMR data were identical with those described in the literature[34].

Conclusion

In this paper, a conjugative addition of aromatic amines to cyclopentenone and cyclohexenone in alkaline Al_2O_3 is reported. This procedure achieves a high yield by using a green and reused solid reaction media, besides, the procedure is easy to handle. These remarkable advantages will make this approach not only suitable for laboratory scale research but also for industrial applications.

ACKNOWLEDGEMENTS

This work was supported by the Research Projects of Zhejiang Provincial Education Department (No. 20070680) and Zhejiang Apeloa Medical Technology Co. Ltd. for financial support.

REFERENCES

1. J.S. Yadav, B.V.S. Reddy, A.K. Basak and A.V. Narsaiah, *Chem. Lett*., **32**, 988 (2003).
2. L.-W. Xu and Y. Li, *Synlett*, 2337 (2003).
3. C. Mukherjee and A.K. Misra, *Lett. Org. Chem*., **41**, 54 (2007).
4. B. Sreedhar, P. Radhika, B. Neelima and N. Hebalkar, *Chem. Asian J*., **3**, 1163 (2008).
5. J.H. Lee, M.-H. Kim, S.-S. Jew, H.-G. Park and B.-S. Jeong, *Chem. Commun*., 1932 (2008).
6. S.W. Kwok, J.E. Hein, V.V. Fokin and K.B. Sharpless, *Heterocycles*, **76**, 1141 (2008).
7. A.K. Verma, P. Attri, V. Chopra, R.K. Tiwari and R. Chandra, *Monatsh. Chem*., **139**, 1041 (2008).
8. A.-G. Ying, L. Liu, G.-F. Wu, G. Chen, X.-Z. Chen and W.-D. Ye, *Tetrahedron Lett*., **50**, 1653 (2009).
9. A.-G. Ying, L.-M. Wang, H.-X. Deng, J.-H. Chen, X.-Z. Chen and W.-D. Ye, *ARKIVOC*, 288 (2009).
10. M.L. Kantam, S. Laha, J. Yadav and S. Jha, *Tetrahedron Lett*., **50**, 4467 (2009).
11. N. Srivastava and B.K. Banik, *J. Org. Chem*., **68**, 2109 (2003).
12. T.C. Wabnitz and J.B. Spencer, *Tetrahedron Lett*., **43**, 3891 (2002).
13. L.-W. Xu, C.-G. Xia and X.-X. Hu, *Chem. Commun*., 2570 (2003).
14. L.-W. Xu and C.-G. Xia, *Tetrahedron Lett*., **45**, 4507 (2004).
15. M.L. Kantam, V. Neeraja, B. Kavita, B. Neelima and M.K. Chaudhuri, *Adv. Synth. Catal*., **347**, 763 (2005).
16. L. Yang, L.-W. Xu, W. Zhou, L. Li and C.-G. Xia, *Tetrahedron Lett*., **47**, 7723 (2006).
17. B.M. Fetterly, N.K. Jana and J.G. Verkade, *Tetrahedron*, **62**, 440 (2006).
18. B. Tamami, A. Fadavi and M. Tamami, *Iran. Polym. J*., **15**, 799 (2006).
19. C. Munro-Leighton, S.A. Delp, E.D. Blue and T.B. Gunnoe, *Organometallics*, **26**, 1483 (2007).
20. M.L. Kantam, M. Roy, S. Roy, M.S. Subhas, B. Sreedhar, B.M. Choudary and R.L. De, *J. Mol. Catal. A: Chem.*, **265**, 244 (2007).
21. S. Kobayashi, K. Kakumoto and M. Sugiura, *Org. Lett*., **4**, 1319 (2002).
22. (a) M.J. Gaunt and J.B. Spencer, *Org. Lett*., **3**, 25 (2001); (b) T.C. Wabnitz, J.-Q. Yu and J.B. Spencer, *Chem. Eur. J*., **10**, 484 (2004); (c) K. Takasu, N. Nishida and M. Ihara, *Synlett*, 1844 (2004); (d) R.S. Jensen, K. Umeda, M. Okazaki and F. Ozawa, *J. Organomet. Chem*., **692**, 286 (2007); (e) A. Hayashi, M. Okazaki and F. Ozawa, *Organometallics*, **26**, 5246 (2007); (f) H.X. Zhang, Y.H. Zhang, L.F. Liu, H.L. Xu and Y.G. Wang, *Synthesis*, 2129 (2005).
23. H. Firouzabadi, N. Iranpoor, M. Jafarpour and A. Ghaderi, *J. Mol. Catal. A: Chem*., **252**, 150 (2006).
24. M. Kawatsura, S. Aburatani and J. Uenishi, *Tetrahedron*, **63**, 4172 (2007).
25. Y.-D. Lin, J.-Q. Kao and C.-T. Chen, *Org. Lett*., **9**, 5195 (2007).
26. G. Smitha and Ch. Sanjeeva Reddy, *Catal. Commun*., **8**, 434 (2007).
27. B.M. Reddy, M.K. Patil and B.T. Reddy, *Catal. Lett*., **126**, 413 (2008).
28. R. Trivedi, P. Lalitha and S. Roy, *Synth. Commun.*, **38**, 3556 (2008).
29. M. Jafarpour, A. Rezaeifard and M. Aliabadi, *Lett. Org. Chem*., **6**, 94 (2009).
30. L.-W. Xu, L. Liand and C.-G. Xia, *Helv. Chim. Acta*, **87**, 1522 (2004).
31. (a) F.-L. Chung, K.R. Roy and S.S. Hecht, *J. Org. Chem*., **53**, 14 (1988); (b) D. Kumar, G. Patel, B.G. Mishra and R.S. Varma, *Tetrahedron Lett*., **49**, 6974 (2008); (c) S.P. Singh, T.V. Kumar, M. Chandrasekharam, L. Giribabu and P.Y. Reddy, *Synth. Commun*., **39**, 3982 (2009).
32. (a) L.-W. Xu, J.-W. Li and C.-G. Xia, *Synlett*., 2425 (2003); (b) H. Firouzabadi, N. Iranpoor and A.A. Jafari, *Adv. Synth. Catal*., **347**, 655 (2005); (c) S.Azad, T. Kobayashi, K. Nakano, Y. Ichikawa and H. Kotsuki, *Tetrahedron Lett*., **50**, 48 (2009).
33. (a) X. Ai, X. Wang, J.n-M. Liu, Z.-M. Ge, T.-M. Cheng and R.-T. Li, *Tetrahedron*, **66**, 5373 (2010); (b) S. Xia, X. Wang, Z.-M. Ge, T.-M. Cheng and R.-T. Li, *Tetrahedron*, **65**, 1005 (2009).
34. J. Lv, H. Wu and Y.M. Wang, *Eur. J. Org. Chem.*, **11**, 2073 (2010).