http://dx.doi.org/10.5012/bkcs.2012.33.5.1556

A Simple and Efficient One-Pot Three-Component Synthesis of Propargylamines Using Bismuth (III) Chloride

Abbas Teimouri,[*] Alireza Najafi Chermahini,[†] and M. Narimani

Department of Chemistry, Payame Noor University (PNU), 19395-4697, Tehran, I. R. of Iran. [*]E-mail: a_teimouri@pnu.ac.ir
[†]Department of Chemistry, Isfahan University of Technology, Isfahan, Iran
Received December 26, 2011, Accepted February 6, 2012

A simple highly versatile and efficient method has been developed for the three-component coupling of aldehydes, amines and alkynes to prepare propargylamines, in the presence of a catalytic amount of $BiCl_3$. The advantages of methods are high yield, mild reaction conditions, no environmental pollution and easy work up procedure.

Key Words : Bismuth (III) chloride, Green synthesis, Propargylamines, Three component reaction

Introduction

The development of synthetic strategies for C-H bond activation is one of the most important areas in organic chemistry.[1] Three-component coupling of the alkyne, aldehyde and the amine (A3 coupling)[2] gave propargylamines, which are versatile synthetic intermediates in organic synthesis and are also important structural elements in natural products and pharmaceutical preparations.[3] They are important building blocks for the synthesis of heterocyclic compounds such as pyrrolidones, oxoazoles and pyrroles *etc*.[4] These compounds have traditionally been synthesized by nucleophilic attack of lithium acetylides or Grignard reagents on imines or their derivatives.[5] However, these reagents must be used in stoichiometric amounts, are highly moisture sensitive, and require strictly controlled reaction conditions. An alternative atom-economical approach to their synthesis is to perform this type of reaction by a catalytic coupling of alkyne, aldehyde, and amine (A3 coupling) by C-H activation.

The alkyne C-H bond can be activated by employing various homogeneous metal catalysts such as gold complexes,[6] silver salts,[7] copper salts,[8] zinc salts,[9] iron salts,[10] $InBr_3$,[11] $InCl_3$,[12] Ir-complexes,[13] Hg_2Cl_2,[14] $NiCl_2$,[15] zirconium[16] and rhenium.[17]

Different heterogeneous catalysts such as AgI,[18] silver nanoparticles,[19] Ag nanoparticles supported by Ni,[20] Cu(I) complexes,[21] copper(I) pyridine bis-(oxazoline) complexes,[22] CuCl,[23] silica-immobilized CuI,[24] silica gel anchored copper chloride,[23] Ni-Y-zeolite,[25] AgY zeolite,[26] copper-zeolites,[27] Zn dust,[28] nanopowder zinc titanate,[29] copper ferrite nanoparticles,[30] copper-nanoparticles,[31] nanocrystalline copper (II) oxide,[32] impregnated copper on magnetite,[33] Nanosize Co_3O_4,[34] nano indium oxide,[35] and Fe_3O_4 nanoparticles,[36] have also been utilized for alkyne C-H activation.

In addition, ultrasonic radiations[37] and microwave[38] have also been used in the presence of Cu(I) salt. Also a variety of chiral ligands have been used in this reaction to gain high asymmetric induction.[39] Thus, the development of improved synthetic methods for the preparation of propargylamines remains an active research area.

In recent years, bismuth(III) derivatives has attracted much attention because of their friendly ecological behavior and its diverse applicability as catalysts in organic synthesis.[40] Compared with transition-metal complexes, bismuth (III) salts are stable in air, relatively nontoxic and inexpensive. It has been explored as powerful catalyst for different reactions, such as Mannich reaction,[41] allylation[42] and Diels-Alder reactions.[43]

In continuation of our investigations on the use of heterogeneous catalysts for fine chemical preparation through multicomponent procedures[44,45] and working with cyclic amines,[46,47] here we present our recent studies on the synthesis of substituted propargylamines *via* three-component reaction between aldehydes, terminal alkynes, and secondary amines in the presence of Bismuth(III) chloride in ethanol.

Experimental

General Remarks. All reagents were purchased from Merck and Aldrich and used without further purification. Products were characterized by spectroscopy data (IR, FTIR, ^{1}H NMR spectra), elemental analysis (CHN) and melting points. A JASCO FT/IR-680 PLUS spectrometer was used to record IR spectra using KBr pellets. NMR spectra were recorded on a Bruker 400 Ultrasheild NMR and DMSO-d_6 was used as solvent. Melting points reported were determined by open capillary method using a Galen Kamp melting point apparatus and are uncorrected. Mass Spectra were recorded on a Shimadzu Gas Chromatograph Mass Spectrometer GCMS-QP5050A/Q P5000 apparatus.

General Procedure for the Synthesis of Propargylamine Derivatives. To a mixture of aromatic aldehydes (1.0 mmol), amines (1.2 mmol) and phenylacetylene (1.5 mmol) in anhydrous ethanol (5 mL) was added Bismuth (III) chloride (10 mol %) and the solution were mixed and stirred at reflux for appropriate time. After completion of the reaction (as monitored by TLC), the ethanol was removed

under vacuum. The crude mixture was purified by flash column chromatography (EtOAc/petroleum ether 1:4) to afford the pure product.

Data for *N*-(1,3-Diphenyl-2-propynyl)piperidine (Table 1, entry 2): FT-IR (KBr): 2930, 2187, 1598, 1486, 1316, 1152, cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 1.36-1.52 (m, 2H), 1.54-1.64 (m, 4H), 2.50-2.64 (m, 4H), 4.80 (s, 1H), 7.28-7.36 (m, 6H), 7.46-7.56 (m, 2H), 7.62-7.66 (m, 2H); MS (*m/z*): 275.17 . Anal. Calcd for $C_{20}H_{21}N$: C, 87.23; H, 7.69; N, 5.09. Found: C, 86.88; H, 7.46; N, 4.84.

Data for 4-(1,3-Diphenyl-prop-2-ynyl)-morpholine (Table 1, entry 4): FT-IR (KBr): 2935, 2175, 1596, 1500, 1318, 1152, cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 2.54-2.64 (m, 4H), 3.65-3.70 (m, 4H), 4.77 (s, 1H), 7.30-7.37 (m, 6H), 7.52 (d, 2H), 7.61 (d, 2H); MS (*m/z*): 277.30; Anal. Calcd for $C_{19}H_{19}NO$: C, 82.28; H, 6.90; N, 4.85. Found: C, 81.98; H, 6.81; N, 5.12.

Data for *N*-[1-(4-Chlorophenyl)-3-phenyl-2-propynyl]-piperidine (Table 1, entry 8): IR (KBr): 2941, 2206, 1678, 1591, 1485, 1402, 1150, 1094 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 1.45-1.55 (m, 2H), 1.52-1.64 (m, 4H), 2.56-2.66 (m, 4H), 4.70 (s, 1H), 7.26-7.33 (m, 5H), 7.44-7.48 (m, 2H), 7.55-7.58 (m, 2H), ESI MS (*m/z*): 309.12. Anal. Calcd for $C_{20}H_{20}ClN$: C, 77.53; H, 6.52; N, 4.52. Found: C, 77.35; H, 6.41; N, 4.35.

Data for *N*-[1-(4-Chlorophenyl)-3-phenyl-2-propynyl] morpholine (Table 1, entry 10): 4o. Yellow oil. IR (film) 2986, 2205, 1608, 1576, 1406, 1148 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 2.63-2.69 (m,4H), 3.67-3.73 (m, 4H), 7.24-7.29 (m, 5H), 7.38-7.43 (m, 2H), 7.48-7.53 (m, 2H), 5.15 (s, 1H); MS *m/z* (%) 311.11. Anal. Calcd for $C_{19}H_{18}ClNO$: C, 73.19; H, 5.82; N, 4.49. Found: C, 73.06; H, 5.49; N, 4.35.

Data for 4'-*N*-Methyl-*N*-[1-(4-chlorophenyl)-3-phenyl-2-propynyl]-piperazine (Table 1, entry 11): IR (KBr): 2938, 2203, 1676, 1594, 1485, 1454, 1403, 1150, 1091 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 2.15 (s, 3H); 2.36 (brs, 4H), 2.55-2.45 (m, 2H), 2.61-2.57 (brs, 2H), 4.99 (s, 1H), 7.40-7.40 (m, 3H), 7.45 (d, 2H), 7.51-7.52 (m, 2H), 7.56 (d, 2H), MS: *m/z* (%): 324.14; Anal. calcd. for $C_{20}H_{21}ClN_2$; C: 73.95, H: 6.52, N: 8.62. Found: C: 73.71, H: 6.33, N: 8.37%.

Data for *N*-[1-(4-Methylphenyl)-3-phenyl-prop-2-ynyl]piperidine (Table 1, entry 32): FT-IR (KBr): 2937, 2176, 1607, 1502, 1320, 1153 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 1.55-1.61 (m, 4H), 1.43-1.45 (m, 2H); 2.34 (s, 3H), 2.44-2.56 (m, 4H), 4.72 (s, 1H), 7.15 (d, 2H), 7.30 (d, 2H), 7.35-7.47 (m, 5H), MS *m/z* (%) 289.15; Anal. Calcd for $C_{21}H_{23}N$: C, 87.15; H, 8.01; N, 4.84. Found: C, 86.89; H, 8.04; N, 4.56.

Data for *N*-[1-(4-Methoxyphenyl)-3-phenyl-2-propynyl]-piperidine (Table 1, entry 38): Oil. IR (film) 2988, 2187, 1610, 1515, 1325, 1153 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 1.42-1.51 (m, 2H), 1.52-1.76 (m, 4H), 2.55-2.70 (m, 4H), 3.80 (s, 3H), 4.75 (s, 1H), 6.91-6.98 (m, 2H), 7.30-7.40 (m, 3H), 7.51-7.65 (m, 4H); MS *m/z* (%) 305; Anal. Calcd for $C_{21}H_{23}NO$: C, 82.58; H, 7.59; N, 4.59. Found: C, 82.41; H, 7.46; N, 4.37.

Results and Discussion

In an effort to develop an optimal catalytic system, various reaction parameters like effect of temperature, catalyst loading, solvent and time were studied for the preparation propargylamines *via* reaction of benzaldehyde, piperidine and phenylacetylene in solvent under reflux and the results are summarized in Table 1.

The control experiments for the three-component reaction conducted under identical conditions and devoid of $BiCl_3$ gave no coupled product, despite prolonged reaction times.

Various Bi-based catalysts such as $Bi(OTf)_3{\cdot}4(H_2O)$, $Bi(OAc)_3$ and $Bi(NO_3)_3{\cdot}5(H_2O)$ were screened for the three-component reaction. $BiCl_3$ was found to be the most effective catalyst that afforded excellent yield (Table 1, entry 5). The lower catalytic activities of $Bi(OTf)_3{\cdot}4(H_2O)$, $Bi(OAc)_3$ and $Bi(NO_3)_3{\cdot}5(H_2O)$, may be due to their filled coordination sites that hardly interact with C-H bond of the alkyne (Table 1, entries 9 and 10). The $BiCl_3$ can binds with the C-H bond of the terminal alkyne effectively showing better catalytic performance (Scheme 1).

In a systematic study (Table 1), phenylacetylene was added to a solution of benzaldehyde, piperidine and $BiCl_3$ in ethanol and the reaction mixture was stirred for 10 h at room temperature or 5 h at refluxing. Our initial experiments focused on the optimization of the amount of $BiCl_3$ by using 1 equiv of benzaldehyde, 1.2 equiv of piperidine, 1.5 equiv of phenylacetylene and variable amount of $BiCl_3$. It was found that in absence of catalyst no conversion to product was obtained even after 10 h at room temperature.

To investigate the effect of catalyst amount, the model reaction was carried out in the presence of different values of catalyst (2, 5, 8, 10, 15, 20 and 25 mol %).

We observed that 10 mol % of $BiCl_3$ (based on benzaldehyde) could effectively catalyze the reaction with 2 and 5 mol % of $BiCl_3$, a lower yield was observed under the same reaction time (Table 1, entry 2-3) and increasing the amount of $BiCl_3$ to 15, 20 and 25 mol % showed no substantial improvement in the yield (Table 1, entry 4-6).

Table 1. Effect of catalyst type and amount of catalyst on the synthesis of compounds

Entry	Catalyst	Catalyst (mol %)	Time (h)	Yield (%)[a]
1	None	-	48	No reaction
2	$BiCl_3$	2	15	70
3	$BiCl_3$	5	15	75
4	$BiCl_3$	8	15	82
5	$BiCl_3$	10	15	95
6	$BiCl_3$	15	15	70
7	$BiCl_3$	20	15	65
8	$BiCl_3$	25	15	50
9	$Bi(OAc)_3$	15	15	40
10	$Bi(OTf)_3$	15	15	45
11	$Bi(NO_3)_3{\cdot}5(H_2O)$	15	15	30

[a]Yields after isolation of products

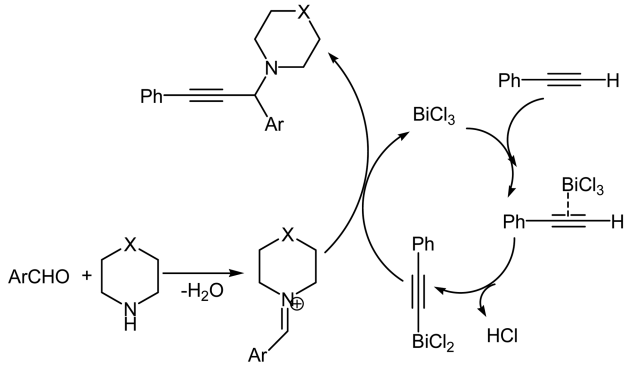
Table 2. Solvent studies under different parameters for the model reaction catalyzed by $BiCl_3$

Entry	Solvent	Time (h)/Yield (%)[a] Room temperature	Time (h)/Yield (%)[a] Reflux
1	H_2O	10/0	5/75
2	EtOH	10/0	5/90
3	MeOH	10/0	5/70
4	CH_3CN	10/0	5/80
5	DCM	10/0	5/65
6	DMF	10/0	5/20
7	THF	10/0	5/45
8	Toluene	10/0	5/35

aromatic aldehydes (1.0 mmol), amines (1.2 mmol) and phenylacetylene (1.5 mmol) in the presence of catalyst (32 mg, 10 mol %) at room temperature and reflux condition in various solvents.

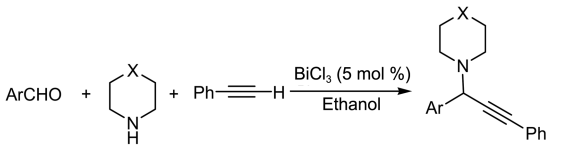
To check the solvent effect on the outcome of the reaction, the above model reaction was carried out with 10 mol % of $BiCl_3$ in solvents such as H_2O, EtOH, CH_3CN, DCM, DMF, THF and Toluene. (Table 2). Acetonitrile and ethanol provided excellent yields and proved to be the solvent of choice. It was observed that much better yield was obtained when the reaction was carried out in ethanol at other solvents (Table 2, entry 2) whereas MeOH and dichloromethane afforded lower yields. The reaction in THF afforded very poor yields whilst the use of DMF and toluene could not effectively catalyze the reaction. Various functionalities present in the aryl aldehydes, such as halogen, methoxy, methyl, hydroxyl and nitro groups were tolerated. The results in Table 3 indicate that the aromatic aldehydes with both electron-donating and electronwithdrawing substituents displayed high reactivity and generatedthe desired products in good to excellent yields. This can be ascribable to the fact that the iminium ion formation from the aldehyde and the secondary amine (first step of the reaction) is very fast and it is independent from the nature of the aromatic aldehydes.

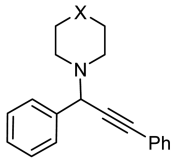
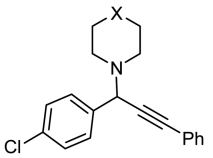
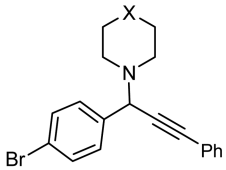
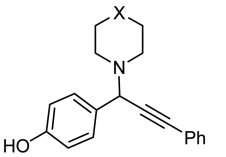
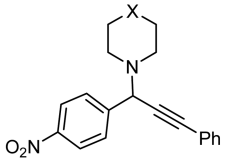
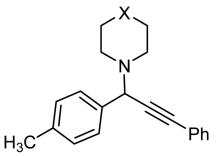
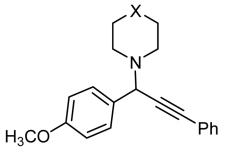
To extend the scope of the reaction, various cyclic secondary amines such as pyrrolidine, piperidine, hexamethyleneimine, morpholine, pyrrolidine, *N*-methyl piperazine, and 4-methyl piperidine, were used and tolerated well (Table 3).



Scheme 1. A tentative mechanism for synthesis of propargylamines in the presence of $BiCl_3$.

Table 3. $BiCl_3$-catalyzed synthesis of propargylamines derivatives[a]



Entry	X	Product	Time (min)	Yield (%)[a]
1	bond		100	85
2	$-CH_2$		80	83
3	$-CH_2CH_2-$		65	75
4	O		110	72
5	$-NCH_3$		90	75
6	$-CHCH_3$		75	82
7	bond		100	80
8	$-CH_2$		80	84
9	$-CH_2CH_2-$		65	81
10	O		110	75
11	$-NCH_3$		90	72
12	$-CHCH_3$		75	86
13	bond		100	70
14	$-CH_2$		80	85
15	$-CH_2CH_2-$		65	83
16	O		110	72
17	$-NCH_3$		90	76
18	$-CHCH_3$		75	84
19	bond		100	80
20	$-CH_2$		80	75
21	$-CH_2CH_2-$		65	80
22	O		110	85
23	$-NCH_3$		90	70
24	$-CHCH_3$		75	55
25	bond		100	75
26	$-CH_2$		80	82
27	$-CH_2CH_2-$		65	87
28	O		110	70
29	$-NCH_3$		90	73
30	$-CHCH_3$		75	75
31	bond		100	72
32	$-CH_2$		80	80
33	$-CH_2CH_2-$		65	83
34	O		110	82
35	$-NCH_3$		90	88
36	$-CHCH_3$		75	87
37	bond		100	75
38	$-CH_2$		80	85
39	$-CH_2CH_2-$		65	86
40	O		110	82
41	$-NCH_3$		90	78
42	$-CHCH_3$		75	85

On the basis of these results, together with the literature reports.[15,30,31,33,35] A tentative mechanism for the $BiCl_3$-catalyzed aldehyde-alkyne-amine coupling is proposed in Scheme 1. The reaction involving the activation of the C-H bond of alkyne by $BiCl_3$. The Bi-acetylide intermediate generated by the reaction of acetylene and $BiCl_3$ reacted with the iminium ion generated in situ from aldehyde and secondary amines to give the corresponding propargylamine.

Conclusions

In conclusion, we have successfully introduce a simple and efficient method for the three-component coupling of aldehydes, cyclic amines and alkynes in ethanol to synthesis of propargylamines in moderate to very good yields using Bismuth (III) chloride. This protocol is an environmentally friendly process and can be used to generate a diverse range of acetylenic amines in good to excellent yields. The simple procedure for catalyst preparation, easy recovery and reusability of the catalyst are expected to contribute to its utilization for the development of benign chemical processes and products.

Acknowledgments. Supports from the Payame Noor University in Isfahan research council and helps of Yasouj University are gratefully acknowledged.

References

1. (a) Dyker, G. *Handbook of C-H Transformations*; Wiley-VCH: Weinheim, 2005; (b) Dyker, G. *Angew. Chem., Int. Ed*. **1999**, *38*, 1698.
2. (a) Wei, C.; Li, Z.; Li, C. J. *Org. Lett.* **2003**, *5*, 4473. (b) Wei, C.; Li, C. J. *J. Am. Chem. Soc.* **2003**, *125*, 9584.
3. (a) Matyus, P.; Dajka-Halasz, B.; Foldi, A.; Haider, N.; Barlocco, D.; Magyar, K. *Curr. Med. Chem.* **2004**, *11*, 1285. (b) Miura, M.; Enna, M.; Okuro, K.; Nomura, M. *J. Org. Chem.* **1995**, *60*, 4999. (c) Naota, I.; Takaya, H.; Murahashi, S. I. *Chem. Rev.* **1998**, *98*, 2599. (d) Zimmermann, K.; Waldmeier, P. C.; Tatton, W. G. *Pure Appl. Chem.* **1999**, *71*, 2039.
4. Boulton, A. A.; Davis, B. A.; Durden, D. A.; Dyck, L. E.; Juorio, A. V.; Li, X. M.; Paterson, I. A.; Yu, P. H. *Drug Dev. Res.* **1997**, *42*, 150.
5. (a) Jung, M. E.; Huang, A. *Org. Lett.* **2000**, *2*, 2659. (b) Murai, T.; Mutoh, Y.; Ohta, Y.; Murakami, M. J. *Am. Chem. Soc.* **2004**, *126*, 5968.
6. Lo, V. K. Y.; Liu, Y.; Wong, M. K.; Che, C. M. *Org. Lett.* **2006**, *8*, 1529.
7. (a) Ji, J.-X.; Au-Yeung, T. T. L.; Wu, J.; Yip, C. W.; Chan, A. S. C. *Adv. Synth. Catal.* **2004**, *346*, 42.
8. (a) Shi, L.; Tu, Y.-Q.; Wang, M.; Zhang, F.-M.; Fan, C.-A. *Org. Lett.* **2004**, *6*, 1001. (b) Huma, H. Z. S.; Halder, R.; Karla, S. S.; Das, J.; Iqbal, J. *Tetrahedron Lett.* **2002**, *43*, 6485. (c) Kabalka, G. W.; Wang, L.; Pagni, R. M. *Synlett* **2001**, 676. (d) Wei, C.; Li, C.-J. *J. Am. Chem. Soc.* **2002**, *124*, 5638. (e) Wei, C.; Mague, J. T.; Li, C. *J. Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 5749. (f) Gommarman, N.; Koradin, C.; Polborn, K.; Knochel, P. *Angew. Chem., Int. Ed.* **2003**, *42*, 5763. (g) Colombo, F.; Benaglia, M.; Orlandi, S.; Usuelli, F. *J. Mol. Catal. A: Chem.* **2006**, *260*, 128. (h) Gommermann, N.; Knochel, P. *Chem. Eur. J.* **2006**, *12*, 4380. (i) Bisai, A.; Singh, V. K. *Org. Lett.* **2006**, *8*, 2405. (j) Li, C.-J.; Wei, C. *Chem. Commun.* **2002**, 268. (k) Park, S. B.; Alper, H. *Chem. Commun.* **2005**, 1315. (l) Black, D. A.; Arndtsen, B. A. *Tetrahedron* **2005**, *61*, 11317. (m) Taylor, A. M.; Schreiber, S. L. *Org. Lett.* **2006**, *8*, 143. (g) Gommermann, N.; Knochel, P. *Chem. Commun*. **2004**, 2324. (i) Gommermann, N.; Knochel, P. *Synlett* **2005**, 2799. (j) Colombo, F.; Benaglia, M.; Orlandi, S.; Usuelli, F.; Celentano, G. *J. Org. Chem.* **2006**, *71*, 2064.
9. (a) Ramu, E.; Varala, R.; Sreelatha, N.; Adapa, S. R. *Tetrahedron Lett.* **2007**, *48*, 7184. (b) Frantz, D. E.; Fassler, R.; Carreira, E. M. *J. Am. Chem. Soc.* **1999**, *121*, 11245. (b) Pinet, S.; Pandya, S. U.; Chavant, P. Y.; Ayling, A.; Vallee, Y. *Org. Lett.* **2002**, *4*, 1463. (c) Zani, L.; Alesi, S.; Cozzi, P. G.; Bolm, C. *J. Org. Chem.* **2006**, *71*, 1558. (d) Lee, K.-Y.; Lee, C.-G.; Na, J.-E.; Kim, J.-N. *Tetrahedron Lett.* **2005**, *46*, 69. (e) Jiang, B.; Si, Y.-G. *Tetrahedron Lett.* **2003**, *44*, 6767. (f) Fischer, C.; Carreira, E. M. *Org. Lett.* **2004**, *6*, 1497. (g) Jiang, B.; Si, Y.-G. *Angew. Chem., Int. Ed.* **2004**, *43*, 216.
10. Chen, W. W.; Nauyen, R. V.; Li, C. J. *Tetrahedron Lett.* **2009**, *50*, 2895.
11. Jadav, J. S.; Reddy, B. V. S.; Gopal, A. V. H.; Patil, K. S. *Tetrahedron Lett.* **2009**, *50*, 3993.
12. Zhang, Y.; Li, P.; Wang, M.; Wang, L. *J. Org. Chem.* **2009**, *74*, 4364.
13. Fischer, C.; Carreira, E. M. *Org. Lett.* **2001**, *3*, 4319. (b) Sakaguchi, S.; Kubo, T.; Ishii, Y. *Angew. Chem., Int. Ed.* **2001**, *40*, 2534. (c) Sakaguchi, S.; Mizuta, T.; Furuwan, M.; Kubo, T.; Ishii, Y. *Chem. Commun.* **2004**, 1638.
14. Hua, L. P.; Lei, W. *Chin. J. Chem.* **2005**, *23*, 1076.
15. Samai, S.; Nandi, G. C.; Singh, M. S. *Tetrahedron Lett.* **2010**, *51*, 5555.
16. (a) Traverse, J. F.; Hoveyda, A. H.; Snapper, M. L. *Org. Lett.* **2003**, *5*, 3273. (b) Akullian, L. C.; Snapper, M. L.; Hoveyda, A. H. *Angew. Chem., Int. Ed*. **2003**, *42*, 4244.
17. Kuninobu, Y.; Inoue, Y.; Takai, K. *Chem. Lett.* **2006**, *35*, 1376.
18. (a) Reddy, K. M.; Babu, N. S.; Prasad, P. S. S.; Lingaiah, N. *Tetrahedron Lett.* **2006**, *47*, 7563. (c) Zhang, X.; Corma, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 4358. (d) Li, P.; Wang, L.; Zhang, Y.; Wang, M. *Tetrahedron Lett*. **2008**, *49*, 6650.
19. Yan, W.; Wang, R.; Xu, Z.; Xu, J.; Lin, L.; Shen, Z.; Zhou, Y. *J. Mol. Catal. A: Chem.* **2006**, *255*, 81.
20. Wang, S.; He, X.; Song, L.; Wang, Z. *Synlett* **2009**, 447.
21. (a) Li, P.; Wang, L. *Tetrahedron* **2007**, *63*, 5455. (b) Choudary, B. M.; Sridhar, C.; Kantam, M. L.; Sreedhar, B. *Tetrahedron Lett.* **2004**, *45*, 7319. (c) Wang, M.; Li, P.; Wang, L. *Eur. J. Org. Chem.* **2008**, 2255.
22. Bisai, A.; Singh, V. K. *Tetrahedron* **2011**, In Press
23. Sreedhar, B.; Reddy, P. S.; Krishna, C. S. V.; Babu, P. V. *Tetrahedron Lett.* **2007**, *48*, 7882.
24. Likhar, P. R.; Roy, S.; Roy, M.; Subhas, M. S.; Kantam, M. L.; De, R. L. *Synlett* **2007**, 2301.
25. Namitharan, K.; Pitchumani, K. *Eur. J. Org. Chem.* **2010**, 411.
26. Maggi, R.; Bello, A.; Oro, C.; Sartori, G.; Soldi, L. *Tetrahedron* **2008**, *64*, 1435.
27. Patil, M. K.; Keller, M.; Reddy, B. M.; Pale, P.; Sommer, J. *Eur. J. Org. Chem*. **2008**, 4440.
28. Kantam, M. L.; Balasubrahmanyam, V.; Kumar, K. B. S.; Venkanna, G. T. *Tetrahedron Lett.* **2007**, *48*, 7332.
29. Mukhopadhyay, C.; Rana, S. *Catal. Commun.* **2009**, *11*, 285.
30. Kantam, M. L.; Yadav, J.; Laha, S.; Jha, S. *Synlett* **2009**, 1791.
31. Kidwai, M.; Bansal, V.; Mishra, N. K.; Kumar, A.; Mozumdar, S. *Synlett* **2007**, 1581.
32. Kantam, M. L.; Laha, S.; Yadav, J.; Bhargava, S. *Tetrahedron Lett.* **2008**, *49*, 3083.
33. Aliaga, M. J.; Ramon, D. J.; Yus, M. *Org. Biomol. Chem.* **2010**, *8*, 43.
34. Bhatte, K. D.; Sawant, D. N.; Deshmukh, K. M. Bhanage, B. M. *Catal. Commun.* **2011**, *16*, 114.
35. Rahman, M.; Bagdi, A. Kr.; Majee, A.; Hajra, A. *Tetrahedron Lett.* **2011**, *52*, 4437.
36. Sreedhar, B.; Suresh Kumar, A.; Reddy, P. S. *Tetrahedron Lett*.

2010, *51*, 1891.
37. Sreedhar, B.; Reddy, P. S.; Prakash, B. V.; Ravindra, A. *Tetrahedron Lett*. **2005**, *46*, 7019.
38. (a) Leadbeater, N. E.; Torenius, H. M.; Tye, H. *Mol. Divers*. **2003**, *7*, 135. (b) Du, W. Q.; Zhang, J. M.; Wu, R.; Liang, Q.; Zhu, S. Z. *J. Fluorine Chem*. **2008**, *129*, 695.
39. Alakesh, B.; Vinod, K. S. *Org. Lett.* **2006**, *8*, 2405.
40. (a) Leonard, N. M.; Wieland, L. C.; Mohan, R. S. *Tetrahedron* **2002**, *58,* 8373. (b) Matano, Y.; Ikegami, T. In *Organobismuth Chemistry*; Suzuki, H., Manato, Y., Eds.; Elsevier: New York, 2001; Chapter 2; pp 21-245. (c) De, S. K.; Gibbs, R. A. *Tetrahedron Lett.* **2004**, *45*, 7407. (d) Suzuki, H.; Ikegami, T.; Matano, Y. *Synthesis* **1997**, 249. (e) Soleimani, E.; Khodaei, M. M.; Koshvandi, A. T. K. *Chinese Chem. Lett.* **2011**, *22*, 927.
41. Li, H.; Zeng, H.; Shao, H. *Tetrahedron Lett*. **2009**, *50*, 6858.
42. De, S. K.; Gibbs, R. A. *Tetrahedron Lett*. **2005**, *46*, 8345.
43. (a) Sabitha, G.; Reddy, E. V.; Maruthi, C.; Yadav J. S. *Tetrahedron Lett.* **2002**, *43*, 1573. (b) Sabitha, G.; Reddy, E. V.; Yadav, J. S.; Krishna, K. V. S.; Sankar, R. *Tetrahedron Lett.* **2002**, *43*, 4029. (c) Li, Z.; Wei, C.; Chen, L.; Varma, R. S.; Li, C. J. *Tetrahedron Lett.* **2004**, *45*, 2443.
44. Teimouri, A.; Najafi Chermahini, A. *Journal of Molecular Catalysis A: Chemical* **2011**, *346*, 39.
45. Teimouri, A.; Najafi Chermahini, A. *Arabian Journal of Chemistry*, In Press, Corrected Proof, Available online 2 June 2011.
46. Dabbagh, H. A.; Teimouri, A.; Najafi Chermahini, A.; Shiasi, R. *Spectrochimica Acta Part A* **2007**, *67*, 437.
47. Dabbagh, H. A.; Teimouri, A.; Najafi Chermahini, A. *Applied Catalysis B: Environmental.* **2007**, *76*, 24.