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BNBTS More than Brominating Agent: Green and One-pot Route for the C-N Bond Formation in Water from Alkenes

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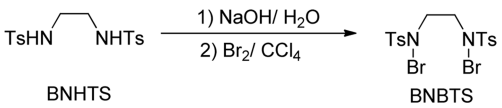
In this paper, in addition to introducing efficient method for bromohydrin and bromoether preparation, simple, green and efficient method to C-N bond formation from alkene and *N,N'*-Dibromo-*N,N'*-1,2-ethanediyl-bis(*p*-toluenesulfonamide) [BNBTS] in water was investigated. The reaction between alkenes, β-cyclodexterin, and BNBTS took place in water afterward, by making media basic; it will give the corresponding valuable building blocks in good yields (45-79%).

Key Words : C-N bond formation, BNBTS, *N*-bromo sulfonamide, Bromo hydrin, Building blocks

Introduction

The regioselective electrophilic addition to alkenes is of importance process in organic synthesis and several methodologies have been described in the literature. The transformation of alkenes into the corresponding halohydrins and haloethers is frequently practiced in organic synthesis.[1] Cohalogenation is one of the most regularly used methods, among these methodologies. This method includes halogenation of an alkene in the presence of a nucleophilic solvent such as alcohol, water, carboxylic acid, *etc*.[2] Bromohydrin and bromoether derivatives are important synthons[3] which are also widely applicable in industrial processes for synthesis of drugs, pharmaceuticals, agrochemicals, pigments and photographic materials.[4] Classical methodologies involved addition of alcohols and water into alkenes, mediated by variety of metal salts[5] or oxidizing reagents.[6] Also, alternative methodologies for synthesis of bromohydrin and bromoether derivatives are widely used by the reaction of alkenes with TBCA,[7] SMBI,[8] *N*-bromosaccharin,[9] and $TsNBr_2$ 10. However, these methods often involve using expensive reagents, difficult conditions for preparation of reagents, longer reaction times and formation of a variety of by-products which result low yields 11. Herein, synthesis of bromohydrins and bromoethers using BNBTS reagent and catalytic amount of ammonium acetate is put into experiment. *N,N'*-Dibromo-*N,N'*-1,2-ethanediyl-bis(*p*-toluenesulfonamide) [BNBTS], synthesized *via* direct bromination of *N,N'*-1,2-ethanediyl-bis(*p*-toluenesulfonamide) [BNHTS][12] (Scheme 1).

BNBTS can be applied in halogenations reactions, formation and cleavage of carbon-heteroatom bonds, oxidation reactions and some other miscellaneous reactions.[13] This reagent has some advantageous features: The preparation of BNBTS is easy, it is stable for several months under atmospheric conditions, and the products of reaction with BNBTS are simply isolated by filtering off and are reusable for many times without any serious decrease in yield.[14] It is found that the presence of NH_4OAc will enhance the reaction rate because of production of the HOAc and HBr would polarize the N-Br bond of *N*-bromo reagents and facilitate the bromination reaction of olefins.[15,16] Ammonium acetate in comparison with other reagents such as PPh_3,[17] CF_3COOH[18] and TMSOTf[19] is highly available and its work up procedure is simple. C-N bond formation, especially *N*-alkylation of sulfonamides is of importance in organic synthesis. In this regard, several methodologies have been described in the literature.[20] The products resulting from these processes are a highly notable group of compounds because of their biological properties such as antitumor, anticonvulsant, anticancer and antifungal activities.[21] Unfortunately, those methods are often involved in using of expensive metal catalysts, difficult conditions, overalkylation and formation of a variety of by-products which results in low yields.



BNHTS BNBTS

Scheme 1. Synthesis of BNBTS.

Experimental

Typical Procedure for Bromohydrin Fromation. To a solution of alkene (1 mmol), solvent (4 ml acetone and 1 mL H_2O) and NH_4OAc (10 mol %), BNBTS (0.6 mmol) was added at room temperature. The reaction was monitored by TlC. After completion of the reaction, the insoluble BNHTS was removed by filtration and washed with Et_2O (15 mL) and the organic phase was dried (anhydrous Na_2SO_4). The solvent was evaporated with a rotatory evaporator, and then purified by column chromatography (SiO_2, hexane, EtOAc). For example 2-Bromo-1-(4-methoxy-Phenyl)-ethanol (14): ^{1}H NMR ($CDCl_3$-400 MHz) δ 3.25 (1H (OH), s), 3.48 (1H, dd, J = 8.4 Hz, J = 10.4 Hz), 3.54 (1H, dd, J = 4 Hz, J = 10.4 Hz) 3.77 (3H, s), 4.8 (1H dd, J = 4 Hz, J = 8.4 Hz), 6.8-7.29

(4H, m). ^{13}C NMR ($CDCl_3$-100.6 MHz) δ 39.7, 55.3, 73.3, 114.0, 127.3, 132.8, 144.1, 159.5. IR (neat): 3432 (OH).

Typical Procedure for Bromoether Formation. To a solution of alkene (1 mmol), solvent (alcohols) and NH_4OAc (10 mol %), BNBTS (0.6 mmol) was added at room temperature. The reaction was monitored by TlC. After completion of the reaction, the insoluble BNHTS was removed by filtration and washed with Et_2O (15 mL) and the organic phase was dried (anhydrous Na_2SO_4). The solvent was evaporated with a rotatory evaporator, and crude product purified by column chromatography (SiO_2; *n*-Hexane, EtOAc 10:1). The solvent was evaporated to give pure bromoether as colorless or light orange oil.

Selected Spectra Data.

1-Bromo-2-ethoxypropan-2-yl) benzene (1b): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.23-1.28 (3H, t), 1.76 (3H, s), 3.36-3.47 (2H, m), 3.55-3.7 (2H, m), 7.27-7.48 (5H, m), ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 16.1, 28.2, 44.9, 71.7, 86.9, 125, 127.6, 128.5, 144.4.

1-Bromo-2-isopropoxypropan-2-yl) benzene (1c): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.16 (d, 3 H, J = 6. 5 Hz), 1.24 (d, 3H, J = 6.5 Hz), 1.69 (3H, s), 3.37-3.46 (2H, dd, J = 10.3 Hz, J = 20 Hz), 3.49 (1H, m), 7.29-7.42 (5H, m).

2-(2-Bromo-1-phenylethoxy) ethanol (7): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.17 (1H (OH), br), 3.4-3.59 (4H, m), 3.65-3.77 (2H, m), 4.51 (1H, dd, J = 4.3 Hz, J = 8.3 Hz), 7.27-7.38 (4H, m). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 36.8, 61.6, 70.5, 82.0, 126.9, 128.5, 128.6, 129.5, 138.5.

General Procedure for the Preparation of bis-sulfonamides (18-22): β-CD (0.15 mmol) was dissolved in water (10 mL) by warming to 60 °C until a clear solution was formed. Alkene (1 mmol) and *N,N′*-dibromo-*N,N′*-1,2-ethanediyl-bis (*p*-toluene sulfonamide) (0.6 mmol) was added to reaction mixture. The reaction was monitored by TLC. After completion of the reaction, was added NaOH (10 mol %) and the mixture stirred at room temperature until the reaction was complete. The reaction was monitored by TLC. The organic material was extracted with ethyl acetate. The organic phase was then dried (anhydrous $MgSO_4$), filtered, and the solvent was removed under vacuum. The products were purified by column chromatography (SiO_2; *n*-Hexane, EtOAc 5:1).

***N,N′*-(Ethane-1,2-diyl)bis(*N*-(2-hydroxy-2-phenylethyl)-4-methylbenzenesulfonamide (18):** Solid; mp 156 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.66 (2H (OH), s), 2.46 (3H, s), 2.66-2.94 (1H, m), 2.98-3.167 (1H, m), 3.42-3.54 (1H, m), 3.65-3.77 (1H, m), 5.15 (1H, dd, J = 7.2 Hz, J = 13.2 Hz), 7.28-7.42 (7H, m), 7.64-7.68 (2H, m). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 21.6, 49.9, 50.2, 51.7, 52.0, 58.0, 58.4, 127.5, 127.5, 128.2, 128.2, 128.9, 129.0, 129.9, 134.7, 134.8, 135.8, 138.8, 144.1. IR (KBr): 1154 (SO_2, sym.), 1348 (SO_2, unsym.), 3447 (OH). Anal. Calcd for $C_{30}H_{32}N_2O_6S_2$: C, 63.13; H, 5.96; N, 4.60% Found: C, 63.09; H, 5.87; N, 4.71%.

***N,N′*-(Ethane-1,2-diyl)bis(*N*-(2-hydroxy-2-(*P*-tolyl)ethyl)-4-methylbenzenesulfonamide (19):** Solid; mp 161 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.29 (2H (OH), s), 2.35 (3H, s), 2.47 (3H, s), 2.76-2.95 (1H, m), 3.08-3.11 (1H, m), 3.44-3.55 (1H, m), 3.65-3.75 (1H, m), 5.154 (1H, dd), 7.16-7.19 (2H, m), 7.29-7.35 (4H, m), 7.66-7.69 (2H, m). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 21.2, 21.6, 50.1, 52.1, 58.2, 127.4, 127.5, 128.0, 128.0, 129.5, 129.6, 129.9, 129.9, 134.7, 134.8, 135.8, 135.8, 144.0. IR (KBr): 1157 (SO_2, sym.), 1344 (SO_2, unsym.), 3446 (OH). Anal. Calcd for $C_{32}H_{36}N_2O_6S_2$: C, 64.13; H, 6.33; N, 4.40%. Found: C, 64.23; H, 6.19; N, 4.51%.

***N,N′*-(Ethane-1,2-diyl)bis(*N*-(2-hydroxy-2-phenylethyl)-4-methylbenzenesulfonamide (20):** Solid; mp 176 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.92 (2H (OH), s), 2.44 (3H, s), 2.39-2.48 (1H, m), 2.91-2.98 (1H, m), 3.09-3.18 (1H, m), 3.57-3.72 (1H, m), 5.13-5.19 (1H, m), 7.25-7.44 (6H, m), 7.61-7.73 (2H, m). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 21.6, 49.8, 50.2, 50.3, 50.7, 57.6, 58.1, 123.0, 123.0, 127.3, 127.04, 129.9, 129.9, 130.0, 132.1, 132.1, 134.5, 134.8, 137.7, 137.8, 144.3. IR (KBr): 1158 (SO_2, sym.), 1336 (SO_2, unsym.), 3291 (OH). Anal. Calcd for $C_{32}H_{34}Br_2N_2O_6S_2$: C, 50.14; H, 4.47; N, 3.65%. Found: C, 50. 06; H, 4.56; N, 3.59%

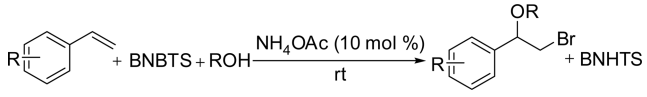
***N,N′*-(Ethane-1,2-diyl)bis(*N*-(2-(4-chlorophenyl)-2-hydroxyethyl)-4-methylbenzenesulfonamide (21):** Solid; mp 174.5 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.63 (2H (OH), s), 2.48 (3H, s), 2.71-2.86 (1H, m), 2.95-3.09 (1H, m), 3.95-3.57 (1H, m), 3.64-3.75 (1H, m), 5.13-5.22 (1H, m), 7.22-7.37 (6H, m), 7.63-7.7 (2H, m). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 21.6, 49.9, 50.9, 57.7, 58.2, 127.3, 127.3, 129.1, 129.1, 129.5, 129.6, 134.4, 134.7, 134.7, 137.2, 137.3, 144.3. IR (KBr): 1157 (SO_2, sym.), 1343 (SO_2, unsym.), 3438 (OH). Anal. Calcd for $C_{30}H_{30}Cl_2N_2O_6S_2$: C, 56.72; H, 5.06; N, 4.13% Found : C, 56.87; H, 4.95; N, 4.21%.

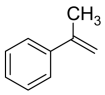
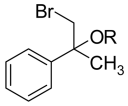
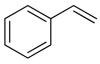
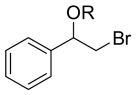
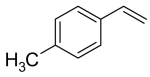
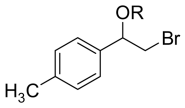
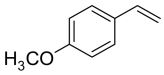
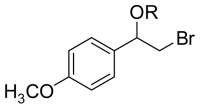
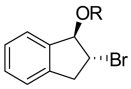
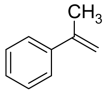
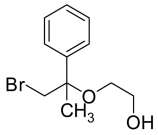
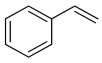
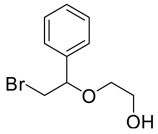
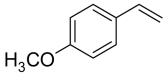
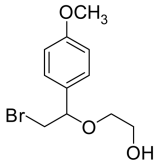
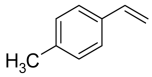
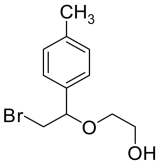
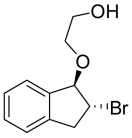
***N,N′*-(Ethane-1,2-diyl)bis(*N*-(2-hydroxy-2-(4-methoxyphenyl)ethyl)-4-methylbenzenesulfonamide (22):** Solid; mp 173.5 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.31 (2H (OH), s), 2.45 (3H, s), 2.85-2.86 (1H, m), 3.3-3.34 (1H, m), 3.56-3.61 (1H, m), 3.73-3.78 (1H, m), 3.81 (3H, s), 5.11 (1H, dd, J = 6.8 Hz, J = 8.8 Hz), 6.81-6.83 (2H, m), 7.08-7.11 (2H, d, J = 12 Hz), 7.55-7.58 (2H, m). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 21.5, 30.4, 44.5, 55.3, 61.5, 114.0, 114.0, 127.1, 127.2, 127.6, 129.5, 129.7, 136.7, 143.7, 159.5. IR (KBr): 1157 (SO_2, sym.), 1340 (SO_2, unsym.), 3446 (OH). Anal. Calcd for $C_{34}H_{40}N_2O_8S_2$: C, 61.06; H, 6.03; N, 4.19%. Found: C, 60.91; H, 6.11; N, 4.24%.

Results and Discussion

In this study, we are aimed in achieving and introducing some new applications of BNBTS reagent in organic transformations. To accomplish this purpose first, reactivity of this reagent was investigated in order to prepare bromohydrins and bromoethers. In this regard, the reaction carried out in the presence of different alcohols (methanol, ethanol, *iso*-propanol, *tert*-buthanol), alkenes, reagent and ammonium acetate as catalyst at room temperature. The corresponding bromoethers with good to excellent yields (79-98%) were obtained in very short times (2-20 min) in this condition (Table 1). Initial experiments were carried out by addition of BNBTS (0.6 mmol) to a solution of the styrene

Table 1. Preparation of bromoether from reaction between alkene with different alcohols and BNBTS in the presence NH_4OAc



Entry	Alkene	ROH	Product	Time (min)	Isolated Yield (%)[a]	Number of product
1		MeOH EtOH *i*-PrOH *t*-BuOH		2 4 7 -	90 90 88 -	1a 1b 1c 1d
2		MeOH EtOH *i*-PrOH *t*-BuOH		3 3 6 20	93 90 87 87	2a 2b 2c 2d
3		MeOH EtOH *i*-PrOH *t*-BuOH		2 3 6 20	93 92 86 89	3a 3b 3c 3d
4		MeOH EtOH *i*-PrOH *t*-BuOH		2 2 4 18	95 95 91 86	4a 4b 4c 4d
5		MeOH EtOH *i*-PrOH *t*-BuOH		3 5 8 20	91 91 85 79	5a 5b 5c 5d
6		Ethylene glycol		35	77	6
7		Ethylene glycol		35	81	7
8		Ethylene glycol		25	83	8
9		Ethylene glycol		30	80	9
10		Ethylene glycol		30	68	10

[a]Isolated yield after column chromatography

(1 mmol) in methanol as a nucleophilic solvent at room temperature. The reaction of styrene with BNBTS took 2.5 h to produce 89% of the corresponding bromoether in methanol as a nucleophilic solvent at room temperature. When this reaction carried out in the presence of NH_4OAc, the reaction was accelerated (it takes only 3 min and it yields 92% product, Entry 1, Table 1). The optimum amount of NH_4OAc was found 10 mol %. It's noteworthy that by increasing the NH_4OAc amount to 30% the reaction yield doesn't change extensively. Additionally, the reaction between derivatives of the glycols (mono, di, tri, tetra) and different alkenes were carried out and ethylene glycol was the best. The corresponding bromoethers were synthesized in acceptable yields (68-83%) *via* reaction of alkenes and ethylene glycol in the presence of BNBTS and NH_4OAc (6-10). A mixture of products were observed, when the reaction was carried out

Table 2. Optimization of solvent for Bromohydrin formation

Entry	Solvent (4:1)	Yield[a] (%)
1	CH_3CN-H_2O	68
2	THF-H_2O	74
3	Acetone-H_2O	92

[a]Isolated yield after column chromatography

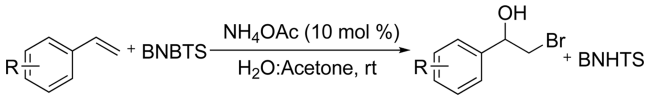
in THF or Et_2O. After optimizing the reaction conditions, a variety of aromatic olefins were reacted in the same conditions as described in Table 1.

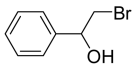
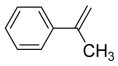
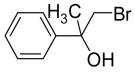
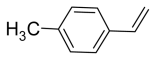
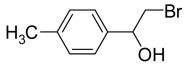
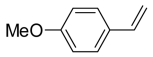
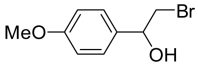
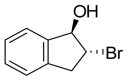
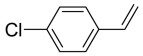
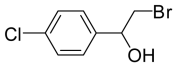
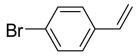
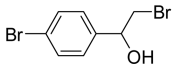
Alkenes were reacted in acetone and water (ratio 4:1) instead of alcohols as nucleophile to give the corresponding bromohydrin with excellent yields (84-95%) at room temperature and short reaction times (2-5 min). This reaction was carried out in the different solvents and acetone showed better result Table 2.

The reactions were clean and all the synthesized products were characterized by their spectra data. The results are shown in Table 3.

In second and much more interesting part of this work, we like to introduce BNBTS as reagent with ability of transfering valuable sulfonamaide moiety to alkenes and preparation of new bis-sulfonamides. For this, the potential of BNBTS for the development of green and efficient method for the C-N bond formation was investigated. In 1955, NBS was used as a brominating agent by Guss and Rosenthal for the synthesis of bromohydrin in water.[22] Besids, Rao *et al*. reported an efficient method for the transformation of alkenes to halohydrins using NXS (X = Br, I) as a halogenating agent in the presence of β-cyclodextrin in water.[23] In this work, water was used instead of organic solvents. Water is a green, available, cheap and safe solvent comparing to organic solvents and it has attracted a lot of attention in organic synthesis. There are some advantages in exploiting water as a solvent includes First of all, it leads to a low cost. Secondly, it makes the reaction condition simple. Thirdly, it makes workup process easy and finally, it is known to enhance the rates and to affect the selectivity of a

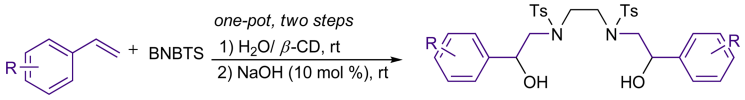
Table 3. Preparation of bromohydrin in the reaction of alkenes with BNBTS in the presence of NH_4OAc

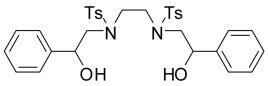
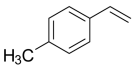
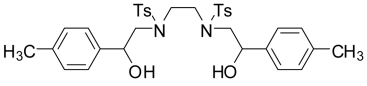
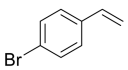
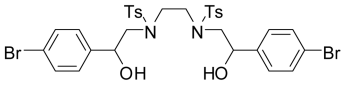
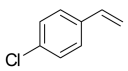
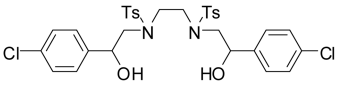
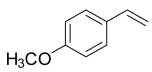
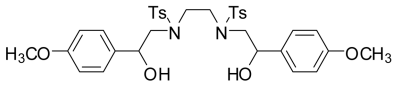


Entry	Alkene	Product	Time (min)	Yield[a] (%)	Number of product
1			4	92	11
2			3	92	12
3			4	89	13
4			2	95	14
5			3	94	15
6			5	84	16
7			4	87	17

[a]Isolated yield after column chromatography.

Table 4. One-pot Synthesis of bis-sulfonamide using β-cyclodextrin and BNBTS in water at room temperature



Entry	Alkene	Product	Time (h)	Yield[a]	Number of product
1			4	75	18
2			3.5	79	19
3			5	56	20
4			5	51	21
5			3	45 [b]	22

[a]Isolated yield after column chromatography. [b]In addition, 40% yield of mono product was isolated after column chromatography.

wide variety of organic reactions. Herein, it was observed that whenever this reaction was carried out in the presence of β-cyclodextrin, the reaction rate in water was enhanced. It is noteworthy that by increasing the β-cyclodextrin amounts to 1 mmol the reaction yield does not change extensively but only the reaction rate increases. During this reaction, yellow color of BNBTS is disappeared immediately. This condition is caused by explanatory precipitation of BNHTS, which was further confirmed by monitoring the reaction progress in TLC. After completion of bromohydrin formation step, NaOH (10 mol %) was added to the reaction mixture, and BNHTS precipitated solid changed to its soluble salt. The reaction mixture was stirred and after the usual workup, the corresponding bis-sulfonamides were obtained (Table 4). These bis-sulfonamides can be prepared in same manner from the corresponding bromohydrin. After optimizing the reaction condition, some aromatic olefins were selected and reacted in the same condition. It is worth to note that all olefins resulted in the di-alkylation as the major product except for the reaction of *p*-methoxystyrene which gives the mixed-products of mono and di-alkylation in approximately same amount (Table 4, Entry 5).

Conclusion

In summary, BNBTS was used as an efficient and excellent reagent for the addition reactions of alkenes. According to this process, corresponding bromohydrins and bromoethers were prepared in good yields and short times under mild condition. In addition, here a convenient route for C-N bond formation using BNBTS as an efficient and excellent reagent for the addition reactions of alkenes was developed. According to this process, corresponding bis-sulfonamides were prepared without any need to metal catalyst, eco-friendly and environmentally benign toward green chemistry and under mild condition. In comparison to the previous works, our procedure has more privilege in the factors of the ease of reagent preparation, simplified and one-pot reaction. In addition BNBTS was introduced as reagent with second fantastic property: bis-sulfonamide transfer reagent in green condition.

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References

1. (a) House, H. O. *Modern Synthetic Reaction*, 2nd. Ed.; Benjamin, W. A., Menlo Park, CA, 1972; pp 432-436. (b) Ishii, Y.; Nishiama, Y.; Hesegawa, A.; Nishio, M.; Takase, K.; Masuda, H. *J. Org. Chem.* **1994**, *59*, 5550.
2. Rodriguez, J.; Dulcere, J. P. *Synthesis* **1993**, 1177.
3. Dolence, D.; Harej, M. *J. Org. Chem*. **2002**, *67*, 312.
4. Erikson, R. E. In Scheuer, P. J., Ed., *Marine Natural Products*; Academic: New York, 1986, Vol. *v*, p. 131.
5. de Mattos, M. C. S.; Sanseverino, A. M. *J. Chem. Res*. **2004**, *638*, and references cited therein.
6. (a) Sels, B. F.; de. Vos, D. E.; Jacobs, P. A. *J. Am. Chem. Soc.* **2001**, *123*, 8350, and references cited therein. (b) Dewkar, G. K.; Narina, S. V.; Sudalai, A. *Org. Lett.* **2003**, *5*, 4501.
7. Ribeiro, R. S.; Esteves, P. M.; de Mattos, M. C. S. *Tetrahedron Lett*. **2007**, *48*, 8747.
8. Sumida, T.; Kikuchi, S.; Imafuku, K. *Synthetic Commun*. **2004**, *34*, 4273.
9. de Souza, S. P. L.; da Silva, J. F. M.; de Mattos, M. C. S. *J. Braz. Chem. Soc.* **2003**, *14*, 832.
10. Phukan, P.; Chakraborty, P.; Kataki, D. *J. Org. Chem*. **2006**, *71*, 7533.
11. Yadav, J. S.; Reddy, B. V. S.; Baishya, G.; Harshavardhan, S. J.; Chary, C. J.; Gupta, M. K. *Tetrahedron Lett*. **2005**, *46*, 3569.
12. Khazaei, A.; Ghorbani-Vaghei, R. *Molecules* **2002**, *7*, 456.
13. Kolvari, E.; Ghorbani-Choghamarani, A.; Salehi, P.; Shirini, F.; Zolfigol, M. A. *J. Iran. Chem. Soc.* **2007**, *4*, 126.
14. Ghorbani-Vaghei, R.; Akbari, S. A.; Zolfigol, M. A.; Mirjalili, B. F.; Bamoniri, A. *Mendeleev. Commun.* **2006**, *55*.
15. Das, B.; Venkateswarlu, K.; Damodar, K.; Suneel, K. *J. Mol. Catal. A: Chem*. **2007**, *269*, 17.
16. Tanemura, K.; Suzuki, T.; Nishida, Y.; Horaguchi, T. *Chem. Commun.* **2004**, 470.
17. Firouzabadi, H.; Iranpoor, N.; Ebrahimzadeh, F. *Tetrahedron Lett*. **2006**, *47*, 1771.
18. Ghorbani-Vaghei, R. *Tetrahedron Lett.* **2003**, *44*, 7529.
19. Chassaing, C.; Haudrechy, A.; Langlois, Y. *Tetrahedron Lett.* **1997**, *38*, 4415.
20. (a) Maclean, D.; Hale, R.; Chen, M. *Org. Lett*. **2001**, *3*, 2997. (b) Hamid, A. S. H. M.; Allen, L. C.; Lamb, W. G.; Maxwell, C. A.; Maytum, C. H.; Watson, A. J. A.; Williams, J. M. J. *J. Am. Chem. Soc*. **2009** *131*, 1766. (c) Zhu, M. W.; Fujita, K.; Yamaguchi, R. *Org. Lett*. **2010**, *12*, 1336. (d) Salvatore, R. N.; Nagle, S. A.; Jung, W. K. *J. Org. Chem*. **2002**, *67*, 674.
21. (a) Ali, H. S. E.; Nassar, F. I.; Badawi, A. M.; Afify, A. S. *Int. J. Genet. Mol. Biol*. **2010**, *5*, 78. (b) Patel, N. B.; Patel, V. N.; Patel, H. R.; Shaikh, F. M.; Patel, J. C. *Acta Pol. Pharm. Drug. Res.* **2010**, *67*, 267. (c) Badawi, A. M.; Ali, H. El-S.; Ismail, D. A. *Aust. J. Basic and Appl. Sci*. **2008**, *2*, 301.
22. Guss, C. O.; Rosenthal, R. *J. Am. Chem. Soc*. **1955**, *77*, 2549.
23. Narender, M.; Reddy, M. S.; Nageswar, Y. V. D.; Rao, K. R. *J. Mol. Catal. A: Chem.* **2006**, *258*, 10.