

One pot Detetrahydropyranylation and Deoxygenation of epoxide to hydroxy olefins by TeCl_2/NaI as a novel reagent

Ganpatdan Charan ^{*1}, Mukesh C Patel¹ and Parimal Chatrabhuji¹

¹Pramukh Swami Science and H D Patel Arts College, Kadi, HNG University
Email: ganpatdancharan@gmail.com

ABSTRACT

TeCl_2/NaI provided an efficient and one-pot deprotection of tetrahydropyranyl ethers in alcohols and phenols and sequel deoxygenation of epoxide to hydroxy olefin at reflux temp. in 15 min. Using TeCl_2/NaI in 1:3 ratio, the reaction gave excellent yield (80-95%) for tetrahydropyranyl deprotections followed by deoxygenation without affecting other functional groups.

KEYWORDS: TeCl_2 : NaI/ detetrahydropyranylation/ Deoxygenation of epoxide

***Corresponding author**

Ganpatdan Charan

Pramukh Swami Science and H D Patel Arts College,

Kadi, HNG University

Email; ganpatdancharan@gmail.com

INTRODUCTION

Epoxidation of organic compounds is well-known in organic and pharmaceutical syntheses to obtain a number of oxygen-containing intermediates.¹ In contrast, the reverse reaction (reductive deoxygenation) of epoxide to alkene is little-known with NaOH/n-BuNBr,² Mo(CO)₆,³ CpTiCl₂/Mg,⁴ PPh₃,⁵ Na/Hg⁶ and NaBH₄.⁷ However, these catalysts have some drawbacks such as low activity, low atom efficiency, tedious work up and moisture sensitive reaction conditions.

The TeCl₂ is used as a non-toxic, inexpensive and mild Lewis acid catalyst in diverse organic synthesis. It was mainly used for the functional groups reduction such as nitrile and nitro groups and as a catalyst in ring cyclization reactions to yield heterocycles: benzoxazoles, quinoxalines, benzimidazoles and allylation of carbonyl compounds.⁸ It was also used as a Lewis acid catalyst for the C-C bond formation, Sonn-Muller reaction, Stephen reduction,⁹ polymerization of L-lactide and trans-esterification reactions. Recent deoxygenation reactions of epoxides to olefins was reported using Co(salane)₂/NaHg,¹⁰ (EtO)₂P(O)TeNa,¹¹ LiI/Amberlyst-15,¹² LReO₃/PPh₃,¹³ MoO(Et₂dtc)₂¹⁴ and ZrCl₄/NaI¹⁵ reagents but these methods have drawbacks like less functional group tolerance, less versatility, low yields, long reaction time and tedious workup. Therefore, the development of simple and efficient reductive deoxygenation methods is of high interest.

Protection and deprotection of the functional groups is the most frequent used strategies in the multi-steps organic syntheses. In particular, the protection and the deprotection of hydroxyl and phenolic groups is extremely important because of its presence of a number of compounds of natural products, biological and synthetic compounds such as carbohydrates, macrolides, peptides, steroids, nucleotides and polyethers.^[16] The protection of hydroxyl groups with 3,4-dihydro-2H-pyran (DHP) is the most common method because of the stability of the product, 2-tetrahydropyranyl ethers (THPEs) in the strong basic conditions such as Grignard reagents, organolithium, metal hydrides, catalytic hydrogenation, alkylating and acylating conditions.^[17] Similarly, methoxymethyl chloride (MOMCl) and acetyl chloride/acetic anhydride (CH₃COCl/Ac₂O) reagents are used for the hydroxyl and phenolic groups protection.^[18] Deprotection of these groups (acetyl, THP and MOM ethers) therefore required efficient methods to avoid the product decomposition and/or loss of other functional groups in the molecules. Several catalytic methods have been explored for the selective deacetylation of alcohols and phenols under acidic and basic conditions. For example, and of detetrahydropyranylation includes protic acids,^[19a-d] Lewis acids like BF₃-etherate,^[5e] LiBr,^[19f] LiBF₄,^[19g] LiOTf,^[19h] LiClO₄,^[19i] Sc(OTf)₃,^[19j] In(OTf)₃,^[19k] I₂,^[19l] InCl₃,^[19m] ZrCl₄,^[19n] CuCl₂,^[19o] NH₄Cl,^[19p] graphite,^[19q] clay materials,^[19r] silica-supported sulfuric acid,^[19s] electrogenerated

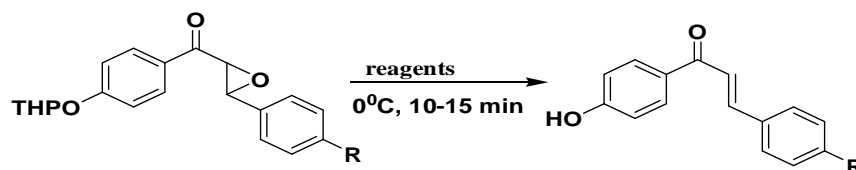
acids,^[19t] bis(trimethylsilyl)sulphate,^[19u] Distannoxane,^[19v] triphenyl phosphine dibromide,^[19w] DDQ,^[19x] and heteropoly acids.^[19y] Similarly, Hence, there is still scope to develop mild and efficient methods in the deacetylation, detetrahydropyranylation and demethoxymethylation of hydroxyl groups.

Herein, we report an efficient one-pot protocol for the deprotection of tetrahydropyranyl ethers and sequel deoxygenation of epoxide to olefin by using novel reagent system.

RESULTS AND DISCUSSION

We screened different metal halide/NaI reagent for the deprotection and sequel deoxygenation as SbCl_3 , InCl_2 , SnCl_2 , SnI_4 , SnBr_4 and MgCl_2 , gave a poor yield (7-40%) at 80°C after 10-15h (Table 1, entries 1- 6 & 8), while, TeCl_2 : NaI gave the optimal yield (95%) using TeCl_2 :NaI (1:3 ratio) in ethanol at 80°C within 15 min (Table 1, entry 5). Therefore, TeCl_2 : NaI (1:3 ratio) in ethanol was selected as an optimized conditions. When, we applied TeCl_2 :NaI (1:0 and 1:2 ratios) in ethanol, got only deprotection product in 95% yields for THP (Table 1, entry 7). The products were confirmed on the basis of their spectral data (supporting information).

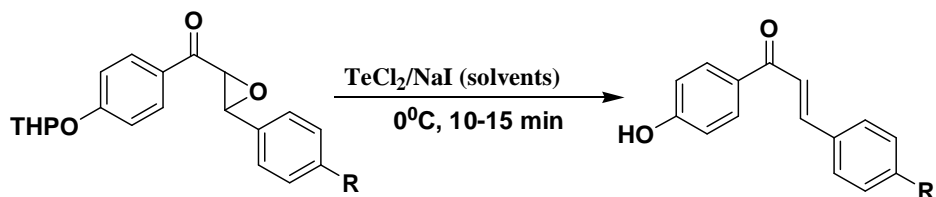
Table 1. Optimization conditions in deprotection and sequel deoxygenation



Entry	Metal halide/NaI	Time	Yield (%)
1	SbCl_3	10-15 h	28
2	SnI_4	6 h	7
3	SbCl_5	10-14 h	20
4	MgCl_2	10-20 h	18
5	SnBr_4	6 h	10
6	InCl_2	4-5 h	10
7	TeCl_2	15 min	95
8	ReCl_2	30 min	40

We observed the solvent effects using solvents like CH₃COCH₃, CHCl₃, CH₂Cl₂, THF, methanol, ethanol and DMSO, where ethanol was found to be the desired solvents gave the maximum yields up to (93%) (Table 2, entry 4). And rest of the solvents mentioned above gave poor yields up to 40%.

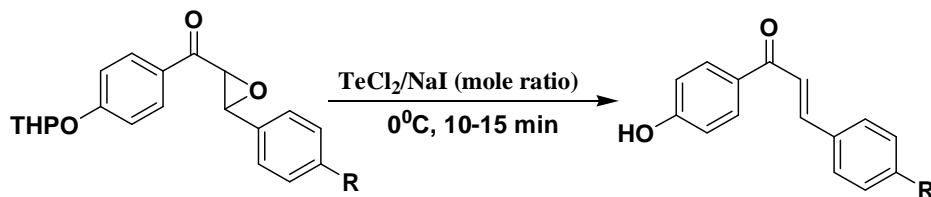
Table 2. Solvents effects in deprotection of tetrahydropyranyl ethers and sequel deoxygenation of epoxide to olefin.



Entry	Solvents	Yield ^a (%)	Yield ^b (%)
1	DCM	30	35
2	Acetone	0	0
3	Methanol	65	80
4	Ethanol	95	93
5	CHCl ₃	50	40
6	DEE	25	20
7	Hexane	0	0
8	NMP	0	0
9	DMF	0	0
10	DMSO	50	40

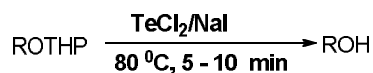
^aYields of detetrahydropyranylation

Under optimized reaction conditions using TeCl₂: NaI, 1:3 ratio, the reaction gave the deprotection and sequeldeoxygenation of epoxide to olefinin excellent yield (95%) within 15 min at 80 °C. (Table 3, entry 3), Interestingly, THP removal and sequel deoxygenation were observed only when we used TeCl₂:NaI,1:3 ratio. On the other hand used of TeCl₂: NaI, 1:0 gave only deprotection (Table 3, entries 1, 2 & 4).

Table 3. Effect of molar ratios of reagent on deprotection of tetrahydropyranyl ethers and sequel deoxygenation of epoxide to olefin.

Entry	TeCl ₂ :NaI (Molar ratio)	Time (Min)	Yield (%)
1	1:0	15	Only deprotection
2	1:2	30-60	Only deprotection
3	1:3	15	95
4	1:4	15	94

Under optimized reaction conditions, the deprotection of tetrahydropyranyl ether of alcohol, phenols and chalcones were highly efficient (Table 4, entries 1-5). Interestingly, THP removal was observed by using novel reagent TeCl₂: NaI in (1:0) to gave compounds **1-5** in excellent yield (90-95%) within 5-10 min at 80°C (Table 3).

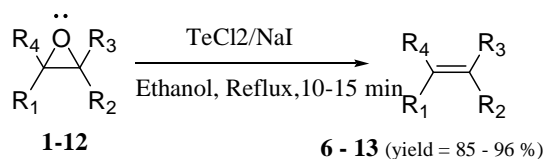
Table 4. Examples of deprotection (only) of acetate, tetrahydropyranyl and methoxymethyl ethers in alcohols and phenols.





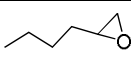





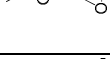


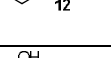


Entry	ROTHP	ROH	Time (min)	Yield ^a (%)
1			5	92
2			7	92
3			5	95
4			8	95
5			10	94

^aIsolated Yields of detetrahydropyranylation, all these product are characterized by comparing their physical and chemical properties with authentic samples.²⁰

Under optimal condition, TeCl_2/NaI reagent was explored for various aliphatic and aromatic epoxides (Table 3). As depicted in table 3, the TeCl_2/NaI reagent surprisingly gave the products **1a-8a** in excellent yield (85-96%) (Table 3, entries 1-8) within 10-15 minutes at reflux temperature. Various aromatic epoxides (Table 3, entries 1 & 7), alicyclic (Table 3, entry 2 & 4) and aliphatic (Table 3, entries 3, 5 & 6) were transformed to alkenes in excellent yield.

Table 5. Deoxygenation of aliphatic and aromatic epoxide by TeCl_2/NaI reagent



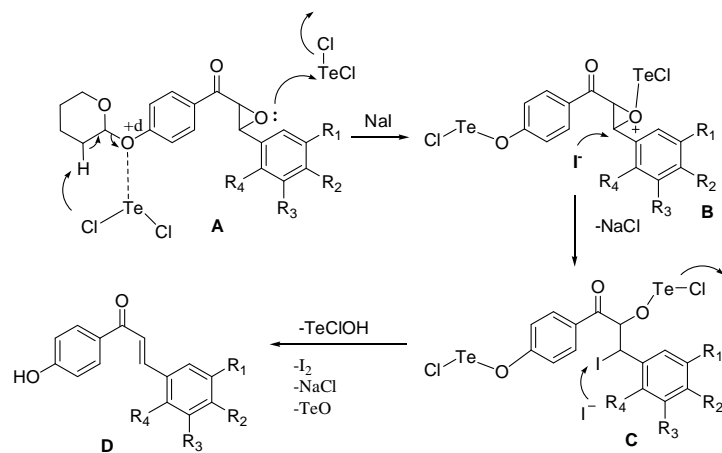
Entry	Epoxides	Product	Time (min) ^a	Yield (%) ^a
1		 6	15	93
2		 7	10	88
3		 8	15	87
4		 9	15	85
5		 10	10	88
6		 11	10	86
7		 12	15	92
8		 13	15	90

^aIsolated yield of deoxygenation, all these product are characterized by comparing their physical and chemical properties with authentic samples.²¹

The carbonyl, nitro, hydroxyl, esters and ketones groups in the deoxygenation of alicyclic epoxides (Table 3, entries 4) and ether linkage in the aliphatic epoxides (Table 3, entries 6) remained unaffected during the reaction. Our method is also highly chemoselective in nature. For example, the chemoselectivity between epoxide ring and hydroxyl group (Table 3, entry 8). All products were characterized by comparing their physical and chemical properties with authentic samples.¹⁷

Detetrahydropyranylation of alcohol and phenols were achieved using TeCl_2/NaI (1:0) in excellent yields (90-95%) within 2-5 min at 80 °C temperature. The presence of other functional groups is tolerated under optimized conditions and Under optimized reaction conditions using $\text{TeCl}_2:\text{NaI}$, 1:3 ratio, the reaction gave the deprotection and sequeldeoxygenation of chalcone epoxide to chalcone in excellent yield (95%) within 15 min at 80 °C. Interestingly, THP removal and sequel deoxygenation were observed only when we used $\text{TeCl}_2:\text{NaI}$, 1:3 ratio. On the other hand used of $\text{TeCl}_2:\text{NaI}$, 1:0 gave only deprotection. The products were characterized on the basis of their spectral analysis ^1H - and ^{13}C -NMR, GC-MS (supporting information). For example, product **14**, the ^1H -NMR spectra showed two characteristic doublet peaks at δ 4.25 & 4.06 ppm ($J = 1.5\text{-}2$ Hz) of the corresponding epoxide ($-\text{CHOCH}-$) disappeared and two protons peak of $-\text{CH}=\text{CH}-$ appeared downfield in aromatic proton region between δ 6.5-8.0 ppm. ^{13}C -NMR spectra, the disappearance of characteristic peak at δ 61.03 & 58.81 ppm of ($-\text{CHOCH}-$) groups and that two protons peaks appeared in downfield region at δ 122.41 & 116.20 ppm and carbonyl peak somewhat shifted downfield compared to corresponding epoxide, indicated deoxygenation of chalcone epoxide to chalcone and presence of IR peak at 3415 cm^{-1} indicates the deprotection of hydroxyl group. These compounds were further characterised by GC-MS.

A proposed mechanism is shown in scheme 1 for THP ether deprotection followed by deoxygenation of chalcone epoxide to olefin, where in compound A ligation of TeCl_2 with THP oxygen resulted in the removal of DHP via intramolecular abstraction of proton Cl ion to give compound B. followed by deoxygenation of chalcone epoxide to olefin, similarly, epoxide oxygen ligated with TeCl_2 might be changed the linear structure of TeCl_2 into v-shaped structure. where a nucleophile attack of oxygen lone pair electrons of epoxide on Te dichloride liberates the chloride ion followed by hydrolysis and epoxide ring opening by iodide ion and removal of the molecular iodine to give the corresponding deprotected olefins. In the deoxygenation reactions consistently brown color was observed due to the generation of molecular iodine, by taking into account this observation, we suggest the plausible reaction mechanism.



Scheme 1. Plausible mechanism for the deprotection followed by deoxygenation of epoxide to olefin by TeCl₂/NaI.

CONCLUSIONS

In conclusion, we have developed an efficient one-pot protocol for the deprotection of tetrahydropyranyl ethers and sequel deoxygenation of epoxide to olefin using reagent TeCl₂:NaI in (1:3 ratio). The reaction gave excellent yield (85-95%) at 80 °C in 10-15 min. However, a selective deprotection of tetrahydropyranyl was afforded using reagent TeCl₂:NaI in (1:0 ratio). This methodology has advantages such as short reaction time, high yields, environment friendly protocol and easy workup procedures.

EXPERIMENTAL SECTION

General methods

Organic solvents were dried by standard methods; the reagents (chemicals) were purchased from commercial sources, and used without further purification. All reactions were monitored by TLC using precoated silica gel aluminum plates. Visualization of TLC plates was accomplished with an UV lamp. Column chromatography was performed using silica gel 60–120 mesh size (RANKEM Limited) with EtOAc–hexanes as eluent. Melting points were recorded on Perfit apparatus and are uncorrected. All products were characterized by NMR, IR and MS spectra. ¹H and ¹³C NMR spectra were recorded in deuterated chloroform (CDCl₃) on a 500 MHz and 125 MHz spectrometer (Bruker), respectively. Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broad (br).

General procedure for deprotection of tetrahydropyranyl ethers of alcohol and phenol:

TeCl₂(1 mmol) was added to a stirred solution of Esters and ethers (1 mmol) in a ethanol, suspension obtained, applied heating to 80°C. After TLC monitoring, the resulting reaction mixture was cool to room temp. and evaporate the solvent by vacuo and extracted with DCM. The organic layer was washed with brine, dried with anhyd.Na₂SO₄, and concentrated in *vacuo* to give the corresponding product which was purified by silica gel column chromatography with hexane-EtOAc eluent to obtain the products **1** to **5**

General procedure for Deoxygenation of aliphatic and aromatic epoxide, followed by deoxygenation of epoxide to olefin by novel TeCl₂/ NaI reagent:

To a solution epoxide (1mmol) and NaI (4mmol) in absolute alcohol (5ml), TeCl₂ (2mmol) was added in a several portions. The mixture was stirred at reflux temperature and the progress of reaction was monitored by TLC. Within 10-15 min the reaction mixture is poured in ice-water, precipitation obtained, stirred for 10 min and filtered the solid, dried to obtain pure products **6-19** with 85-95% yield. (E)-3-(4-fluorophenyl)-1-(4-hydroxyphenyl) prop-2-en-1-one (14)

Yellow solid; Yield: 222 mg (92%);melting point-60-62°C; ¹H NMR (CDCl₃, 500 MHz) δ ppm 7.99(d, *J* = 8.5 Hz, 2H), 7.77 (d, *J* = 15.5 Hz, 1H), 7.62 (dd, *J* = 6, 13.5 Hz, 2H), 7.46 (d, *J* = 15.5 Hz, 1H), 7.10 (t, *J* = 8 Hz, 2H), 6.95 (d, *J* = 8.5 Hz, 2H), 6.24 (s, 1H, br, D₂O exchangeable); ¹³C NMR (CDCl₃, 125 MHz) δ ppm 187.50, 164.68, 162.67, 141.94, 132.02, 131.52, 131.45, 129.53, 122.46, 116.42, 116.25; IR v_{max} (KBr, cm⁻¹): 3415 (OH str), 2931, 2873 (aromatic C-H str), 1681 (C=O str), 1597 (aromatic, C=C str), 1263, 1081, 860, 737; GC-MS (m/z): 242 [M⁺, C₁₅H₁₁FO₂].

ACKNOWLEDGEMENTS

We acknowledge thanks to Research Laboratory, Pramukh Swami Science and H D Patel Arts College, Kadi for providing research facilities.

REFERENCES

1. a) Madesclaire, M. *Tetrahedron***1988**, *44*, 6537; b) Abad, A.; Concepcion, P.; Corma, A.; Garcia, H. *Angew. Chem.Int. Ed.***2005**,*44*, 4066; c) Hayashi, T.; Tanaka, K.; Haruta, M. *J. Catal.* **1998**, *178*, 566; d) Bailie, J. E.; Hutchings, G. *J. Chem. Commun.***1999**, 2151; e) Zhang, X.; Shi. H.; Xu, B.Q. *Angew. Chem., Int. Ed.***2005**,*44*, 7132; e) Girard, P.; Namy, J. L.; Kagan, H.B. *J. Am. Chem. Soc.***1980**,*102*, 2693-2698; f) Concellon, J. M.; Bardales, E. *Org. Lett.***2002**, *4*, 189-191; g) Martin, M. G.; Ganem, B. *Tetrahedron Lett.***1984**,*25*, 251-

- 254; h) Davis, R.E. *J. Org. Chem.* **1958**,23, 1767-1768; i) Neureiter, N. P.; Bordwell, F. G. *J. Am. Chem. Soc.* **1959**,81, 578-580; j) Snyder, H. R.; Stewart, J. M.; Ziegler, J. B. *J. Am. Chem. Soc.* **1947**,69, 2672-2674; k) Aalbersberg, W.G.L.; Vollhardt, K.P.C. *J. Am. Chem. Soc.* **1977**,99, 2792-2794; l) Iranpoor, N.; Kazemi, F. *Synthesis*. **1996**, 821-822; m) Shoppee, C.W.; Sternhell, S.; Taylor, W. C. *Aust.J. Chem.* **1966**,19, 1265; n) Mahesh, M, Murphy, J.A.; Wassel, H, P. *J. Org. Chem.* **2005**,70, 4118; o) Firouzabadi, H.; Iranpoor, N.; Jafapour, M. *Tetrahedron Lett.* **2005**,46, 4107.
2. (a) Silverman, R. B. *J. Am. Chem. Soc.* **1981**,103, 3910; b) Preusch, P. C.; Suttie, J.W. *J. Org. Chem.* **1983**,48, 3301
3. a) Gable, K.P.; Brown, E.C. *Synlett* **2003**, 14, 2243; b) Isobe, H.; Branchaud, B.P. *Tetrahedron Lett.* **1999**, 40, 8747; c) Itoh, T.; Nagano, T.; Sato, M.; Hirobe, M. *Tetrahedron Lett.* **1989**,30, 6387.
4. Marples, B.A.; Muxworthy, J.P.; Baggaley, K.H. *Synlett* **1992**, 646.
5. Csuk, R.; Dorr, P.; *Tetrahedron* **1994**,50, 9983-9998.
6. Yamada, N.; Mizuochi, M. ; Morita, H. *Tetrahedron* **2007**,63, 3408-3414.
7. Kai, K.; Takeuchi, J.; Kataoka, T.; Yokoyama, M.; Watanabe, N. *Tetrahedron* **2008**, 64, 6760-6769.
8. Wang, Z.; Comprehensive Organic Name Reaction and Reagents; John Wiley & Sons, **2010**, 2659.
9. Kundu, A.; Prabhakar, S.; Vairamani, M.; Roy, S. *Organometallics*, **1997**,16, 4796.
10. Isobe, H.; Branchaud, B. P.; *Tetrahedron Lett.* **1999**,40, 8747-8749
11. Clive, D. L.J.; Menchen, S. M. *J. Org. Chem.* **1980**,45, 2347-23544.
12. Righi, G.; Bovicelli, P.; Sperandio, A.; *Tetrahedron* **2000**,56, 1733-1737.
13. Gable, K. P.; Brown, E. C. *Organometallics* **2000**,19, 944-946
14. Moloy, K. G. *Inorg. Chem.* **1988**,27, 677-681.
15. Habib, F.; Nasser, I.; Maasoumeh, J. *Tetrahedron Lett.* 2005, 46(23), 4107-4110.
16. (a) V. Amaranth, A. D. Broom, *Chem. Rev.*, 1977, 77, 183; (b) D. N. Robertson, *J. Org. Chem.*, 1960, **25**, 931.

17. A. R. Hajipour, M. Kargosha, A. E. Ruoho, *Synth. Commun.*, 2009, 39, 1084.
18. (a) T. W. Green, P. G. M. Wuts, *Organic Synthesis*, 3rd ed.; John Wiley: New York, 1999, 306; (b) D. Caine, H. J. Deutsch, *J. Am. Chem. Soc.*, 1978, 100, 8031; (c) M. Isobe, H. Iio, T. Kawai, T. Goto, *J. Am. Chem. Soc.*, 1978, 100, 1942.
19. a) B. Tamami, K. Parvanak, *Tetrahedron Lett.*, 2004, 45, 715; (b) V. V. Namboodiri, R. S. Varma, *Tetrahedron Lett.*, 2002, 43, 1143; (c) B. S. Babu, K. Balasubramanian, *Tetrahedron Lett.*, 1998, 39, 9287; (d) P. N. Reddy, B. K. Sunil, P. S. Kumar, N. Y. Srinivasulu, T. Reddy, B. Rajitha, *Chemistry of Heterocyclic Compounds*, 2005, 41, 11; (e) B. Kumara, A. A. D. Mushtaq Mukherjee, S. S. Chinnib, S. C. Taneja, B. Kumar, *Tetrahedron Lett.*, 2009, 50, 6236; (f) R. R. Diaz, C. R. Melgarejo, M. T. Plaza, I. I. Cubero, *J. Org. Chem.*, 1994, 59, 7928; (g) M. Narender, M. S. Reddy, K. R. Rao, *Synthesis*, 2004, 30, 1741; (h) C. Wiles, P. Watts, S. Haswell, *J. Tetrahedron Lett.*, 2005, 61, 5209; (i) B. Karimi, J. Maleski, *Tetrahedron Lett.*, 2002, 43, 5353; (j) T. Mineno, *Tetrahedron Lett.*, 2002, 43, 7975; (k) B. C. Ranu, M. Saha, *J. Org. Chem.*, 1994, 59, 8269; (l) G. G. Haraldsson, J. E. Baldwin, *Tetrahedron*, 1997, 53, 215; (m) K. Tanemura, T. Haraguchi, T. Suzuki, *Bull. Chem. Soc. Jpn.*, 1992, 65, 304; (n) H. M. S. Kumar, B. V. S. Reddy, E. J. Reddy, J. S. Yadav, *Chem. Lett.*, 1999, 28, 857; (o) J. S. Yadav, D. Srinivas, G. S. Reddy, *Synth. Commun.*, 1998, 28, 1399; (p) A. T. B. Molnarand, *Tetrahedron Lett.*, 1996, 37, 8597; (q) T. Akiyama, H. Shima, S. Ozaki, *Synlett*, 1992, 22, 415; (r) A. R. Srikrishna, J. A. Sattigeri, D. Vijaykumar, *J. Org. Chem.*, 1995, 60, 5961; (s) K. K. Matthew, R. M. Waymouth, *Organometallics*, 2010, 29, 6051; (t) S. Akai, R. Tanaka, H. Hoshi, K. I. Sato, *J. Org. Chem.*, 2013, 78, 8802; (u) S. Syam, S. I. Abdelvahab, M. A. Mamary, M. Syam, *Molecule*, 2012, 17, 6179; (v) G. Sabhita, J. S. Yadav, M. Rajkumar, R. Babu, *Org. Lett.*, 2001, 3, 1149; (w) J. H. Rigby, J. Z. Wilson, *Tetrahedron Lett.*, 1984, 25, 1429; (x) D. R. William, S. Sakdarat, *Tetrahedron Lett.*, 1983, 24, 3965; (y) J. H. Han, Y. E. Kwon, J. H. Sohn, D. H. Ryu, *Tetrahedron*, 2010, 66, 1673.
20. L. Liu, M. Chen, Cai, *Chinese Chemical Letters*, 1992, 8, 585-8.
21. (a) G. A. Russel, G. J. Mikol, in 'mechanism in molecular migration' vol, 1, B. S. Thyagarajan, ed., interscience, New York, N. Y., 1968, pp 157-207; (b) K. B. Sharpless, K. M. Gordon, *J. Am. Chem. Soc.* 1976, 98, 300.
-