DOI: 10.1002/adsc.201000713

Lewis Acid-Catalyzed Oxidative Allylation: A New Approach for the Synthesis of Homoallylic Alcohols and Amines Directly from Alcohols

Vishnu P. Srivastava,[a] Rajesh Patel,[a] and Lal Dhar S. Yadav[a,*]

[a] Green Synthesis Lab, Department of Chemistry, University of Allahabad, Allahabad 211002, India
Fax: (+91)-532-246-0533; phone: (+91)-532-250-0652; e-mail: ldsyadav@hotmail.com

Received: September 19, 2010; Revised: December 16, 2010; Published online: March 10, 2011

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201000713.

Abstract: A new approach for the synthesis of homoallylic alcohols and amines directly from alcohols *via* one-pot sequential oxidation–Barbier reaction and oxidation–condensation–Barbier reactions, respectively, is reported. The protocol involves the one-pot ferric chloride-catalyzed oxidation of alcohols to the corresponding aldehydes with chloramine-T followed by indium-mediated Barbier allylation with allyl bromide to afford homoallylic alcohols in 70–90% overall yields. The ferric chloride-catalyzed condensation of aldehydes and oxidation by-product *p*-toluenesulfonamide followed by indium-mediated Barbier-type allylation of the resulting aldimines with allyl bromide affords homoallylic amines in 60–80% overall yields in the same reaction vessel. The present work demonstrates a new one-pot approach toward homoallylic alcohol and amine synthesis directly from alcohols.

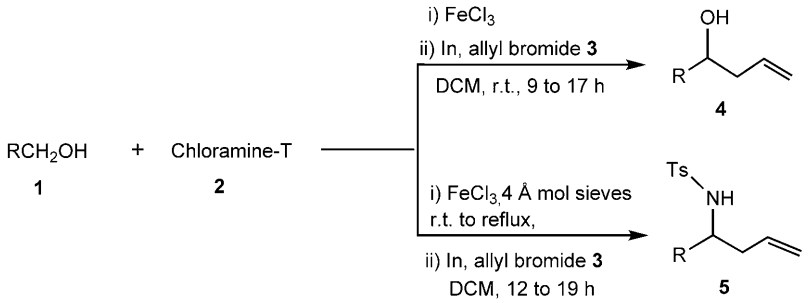
Keywords: alcohols; catalysis; chloramine-T; homoallylic alcohols; Lewis acids; oxidation

Homoallylic alcohols and amines are versatile precursors for various organic transformations. They are used in numerous reactions such as Prins cyclization,[1] β-fragmentation,[2] natural product synthesis,[3] and also represent useful building blocks for the synthesis of biologically and synthetically important compounds[4] such as β-amino acids, 1,3-amino alcohols, 1-amino-3,4-epoxides, pyrrolidines, and piperidines. The coupling of an allyl halide and a carbonyl/imine compound in the presence of a metal is a fundamental procedure for a new C–C bond formation to produce homoallylic alcohols/amines. During the past two decades low-valent metal-mediated allylation of carbonyl/imine compounds to produce homoallylic alcohols/amines has been extensively studied.[5]

Recently, indium has emerged as a metal of high potential in organic synthesis because it has first ionization potential enough low to generate organoindium reagents with organic halides relative to the other metallic elements near it in the periodic table and enough high to resist to boiling water or alkali. Indium does not form oxides readily in air and can be handled safely without apparent toxicity. Indeed, it appears that indium is the most reactive metal for such reactions.

A longstanding endeavour of organic chemists has been to develop methodology to minimize the use of hazardous chemicals, exhaustive, and multi-pot processes. Over the past few decades a lot of work has been done to achieve eco-friendly methodology using green catalysts, solvents, and technology.[6] Recently, a few methods have been developed to replace the direct use of volatile, toxic, or unstable aldehydes with relatively more stable, less volatile, and less toxic alcohols.[7] On the other hand, iron is an abundant, economical, and environmentally friendly metal, which has shown increasing promise as a catalyst in many organic transformations[8] such as oxidation, reduction, condensation, coupling, addition, and substitution reactions.

Meanwhile, the oxidation of alcohols is an important method for forming aldehydes. The oxidation of primary alcohols using different oxidants has been carried out by many workers.[9] However, some of the more historically prominent methods have significant drawbacks.[10] They suffer from difficult work-up, require low temperature, use of solvents that can be difficult to remove, are toxic in nature, and produce hazardous waste. *o*-Iodoxybenzoic acid (IBX) is a mild and selective reagent for this transformation, but its solubility in common solvents remains a problem for which new solutions are still to be sought.[11,12] Advan-



Scheme 1. Direct synthesis of homoallylic alcohols and amines from alcohols.

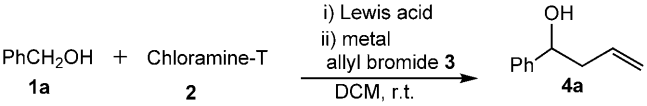
tageously, chloramine-T acts as an oxidizing agent in both acidic and alkaline solutions, and leaves $TsNH_2$ and NaCl as by-products, whose presence would not adversely affect the ensuing Barbier reaction, hence it is a well suited oxidant for the present study. Furthermore, the oxidation by-product $TsNH_2$ could be utilized in the subsequent step to afford *N*-tosylimines, which would be reacted with an allyl halide to obtain homoallylic amines in a one-pot operation.

Several modifications including the use of different metals, catalysts, and solvents have been made to improve the Barbier reaction.[13] Recently, Zhang et al. reported an electrochemical synthesis of homoallylic alcohols from alcohols in a one-pot operation.[13i,j] Consideration of the above valid points and continuation of our quest for developing one-pot protocols,[14] intrigued us to develop a one-pot protocol for the synthesis of homoallylic alcohols/amines starting directly from alcohols employing chloramine-T as the oxidant (Scheme 1).

Our initial experiment was carried out for the reaction of benzyl alcohol (**1a**) with allyl bromide (**3**) using chloramine-T (**2**) as an oxidant at room temperature. A systematic study was first undertaken to define the best reaction conditions and to examine the role of the Lewis acid in the oxidation of alcohol **1a** followed by allylation of the resulting aldehyde in dichloromethane (DCM) as solvent (Table 1). Among the different metals/Lewis acids tested, In/$FeCl_3$ gave the best result (Table 1, entry 1).

The presence of the Lewis acid is extremely important for the oxidation of alcohol **1a** to the corresponding aldehyde (Table 1, entries 7–9). In the absence of a Lewis acid no significant oxidation of alcohol to aldehyde was observed (Table 1, entries 10 and 11, yield of benzaldehyde 8–13%). It was noted that **1a** could not be oxidized to benzaldehyde with a Lewis acid (for example, $FeCl_3$) in the absence of chloramine-T. In addition, the presence of a suitable Lewis acid also accelerates the allylation of the oxidation product significantly (Table 1, entries 4–6 and 10, 11). On the other hand, a combination of Zn/$FeCl_3$ gives a moderate yield of homoallylic alcohol **4a** (Table 1, entry 4) whereas Zn/$ZnCl_2$ gives only a trace of homoallylic alcohols **4a** (Table 1, entry 5). When $CoCl_2$ is used as a catalyst, the oxidation of benzyl alcohol (**1a**) proceeded slowly and a low yield of the aldehyde was obtained but the allylation reaction proceeds smoothly, however, the overall yield is low (Table 1, entry 6).

Table 1. Optimization of catalyst for the synthesis of homoallylic alcohols.[a]

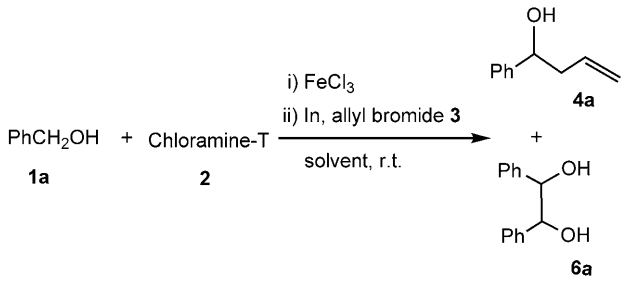


Entry	Metal	Lewis acid[b]	Time [h]	Yield [%][c]
1	In	$FeCl_3$	9	90
2	In	$ZnCl_2$	15	45
3	In	$CoCl_2$	15	57
4	Zn	$FeCl_3$	20	65
5	Zn	$ZnCl_2$	24	trace
6	Zn	$CoCl_2$	20	52
7	–	$FeCl_3$	5	– (95)[d]
8	–	$ZnCl_2$	15	– (50)[d]
9	–	$CoCl_2$	12	– (60)[d]
10	In	–	24	trace[e]
11	Zn	–	30	trace[e]
12	–	$FeCl_3$	5	N.R.[f]

[a] *Reaction conditions:* benzyl alcohol (1 mmol), chloramine-T (1 mmol), DCM (3 mL), In (1 mmol) and allyl bromide (1.5 mmol).
[b] 10 mol% of catalyst.
[c] Yields of the isolated pure compounds.
[d] Isolated yield of benzaldehyde.
[e] Benzaldehyde was formed in 8–13% yield but **4a** was only detected in traces.
[f] No reaction when $FeCl_3$ (1 mmol) was used in the absence of chloramine-T.

The catalytic activity of $FeCl_3$ was also intensively investigated in different solvents. Among the solvents investigated, DCM gave the best result (Table 2, entry 4). In aqueous solvent In/$FeCl_3$ afforded the pinacol coupling product **6a** as the side reaction product along with the Barbier product (Table 2, entry 2). On the other hand, when In/$FeCl_3$ was used in an aprotic solvent, only the Barbier product was obtained (Table 2, entries 1 and 3–7).

Table 2. Optimization of solvent.

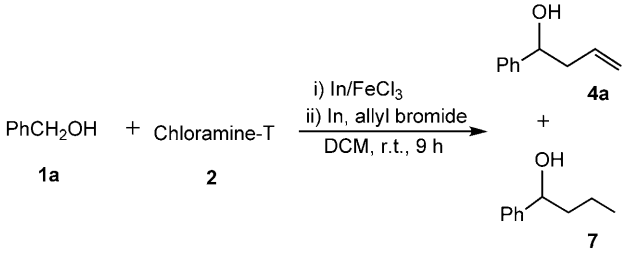


Entry	Solvent	Time [h]	Yield [%][a]
1	THF	20	58
2	THF:H_2O	17	40/(30)[b]
3	toluene	25	30
4	DCM	9	90
5	DMF	15	30
6	CH_3CN	20	62
7	1,4-dioxane	15	38

[a] Yield of isolated pure compound **4a**.
[b] Isolated yield of pinacol **6a**.

Variation of the ratio of metal, Lewis acid, and allyl bromide had a significant impact not only on the conversion but also on the reaction outcome. With 2 equivalents of indium and 3 equivalents of allyl bromide (**3**) in the presence of 10 mol% of $FeCl_3$ the homoallylic alcohol reaction product **4a** was formed along with the reduction product **7** (Table 3, entry 8).

Table 3. Optimization of molar ratio of indium:$FeCl_3$:allyl bromide.



Entry	Indium (equiv.)	$FeCl_3$ (mol%)	Allyl bromide (equiv.)	Yield [%][a]
1	1	10	1.2	83
2	1	10	1.5	90
3	1	10	2	90
4	1	10	3	91
5	1	15	1.5	88
6	1	20	1.5	85
7	1.5	10	3	78 (10)[b]
8	2	10	3	40 (35)[b]
9	2	10	3	– (89)[b,c]

[a] Yields of the isolated pure compound **4a**.
[b] Isolated yield of reduction product **7**.
[c] Reaction time 16 h, yield of **7**.

When the reaction mixture was stirred overnight, the reduction product **7** was obtained as the major product (Table 3, entry 9). The best result was obtained with 1:1.5 ratio of indium and allyl bromide in DCM using 10 mol% of $FeCl_3$ (Table 3, entry 2).

The mechanism for the formation of reduction product **7** presumably involves two steps. In the first step iron(III) chloride is reduced by indium metal to form a low-valent iron species, which in the subsequent step would reduce the allylic alcohol **4a** to the corresponding saturated alcohol **7.** This presumption is in conformity with the earlier reports on the mechanism of reduction using iron(III) chloride and indium metal.[15] It is also supported by the detection of iron(II) in the reaction mixture.

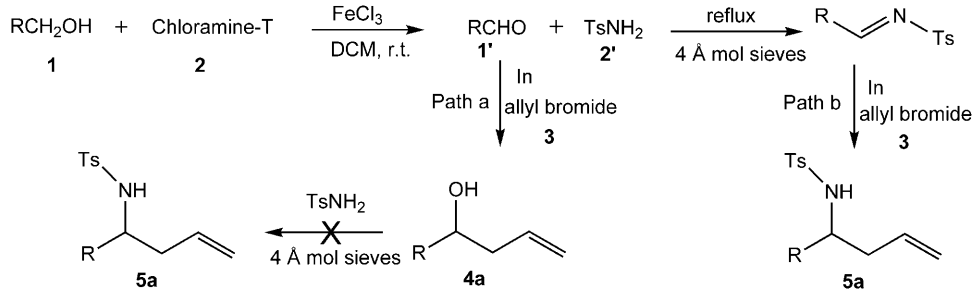
The present optimized synthesis of homoallylic alcohol **4a** involves the stirring of an equimolar mixture of benzyl alcohol and chloramine-T in DCM using $FeCl_3$ as catalyst (10 mol%) at room temperature for 4 h followed by addition of indium powder (1 equiv.) and allyl bromide (1.5 equiv.) and stirring the reaction mixture for 5 h.

The substrate scope was then investigated under the optimized conditions. A variety of alcohols such as substituted benzyl alcohols, 2-furylmethanol, cyclohexylmethanol, and *n*-octanol were tested. For benzyl alcohol and substituted benzyl alcohols containing either electron-withdrawing or electron-donating substituents (Table 4, entries 1–6), the reaction proceeded smoothly and afforded homoallylic alcohols in good to excellent yields. 2-Furylmethanol was transformed into **4g** in 78% yield (Table 4, entry 7) whereas a rela-

Table 4. Synthesis of homoallylic alcohols **4** and amines **5** according to Scheme 1.[a]

Entry	R	Product	Time [h][b]	Yield [%][c,d]
1	Ph	**4a**	9	90
2	*p*-ClC_6H_4	**4b**	10	85
3	*p*-$MeOC_6H_4$	**4c**	11	82
	m-ClC_6H_4	**4d**	10	76
5	*p*-MeC_6H_4	**4e**	9	88
6	*o*-ClC_6H_4	**4f**	14	73
7	2-furyl	**4g**	12	78
8	cyclohexyl	**4h**	17	70
9	*n*-C_7H_{15}	**4i**	16	72
10	Ph	**5a**	12	78
11	*p*-ClC_6H_4	**5b**	15	68
12	*p*-$MeOC_6H_4$	**5c**	14	80
13	*p*-MeC_6H_4	**5d**	13	79
14	*o*-ClC_6H_4	**5e**	19	60

[a] See Experimental Section for general procedure.
[b] Total stirring time.
[c] All the products are known compounds[13] and were characterized by comparison of their mp, TLC, IR and ^{1}HNMR data with those of authentic samples.
[d] Yields of the isolated pure compounds.



Scheme 2. Proposed pathway for the formation of homoallylic alcohols and amines.

tively low conversion of aliphatic alcohols was observed under the present reaction conditions (Table 4, entries 8 and 9).

We also investigated the possibility of substitution of the hydroxy group of homoallylic alcohol **4a** with oxidation by-product *p*-toluenesulfonamide to afford homoallylic amine **5a** under the present reaction conditions by stirring the reaction mixture for 40 h at room temperature and also at reflux in the presence of 4 Å molecular sives, but no appreciable formation of **5a** was observed (Scheme 2, Path a). Then, we turned our attention toward imine formation *via* condensation of the oxidation product aldehyde and the oxidation by-product *p*-toluenesulfonamide followed by the allylation of the resulting imine in the same reaction vessel (Scheme 2, Path b). Thus, stirring an equimolar mixture of benzyl alcohol and anhydrous chloramine-T in the presence of 10 mol% $FeCl_3$ using dry DCM as solvent at room temperature for 4 h followed by addition of 4 Å molecular sieves and reflux for 1.5 h afforded the corresponding imines. Then, the reaction mixture was cooled to room temperature, indium (1 equiv.) and allyl bromide (1.5 equiv.) were added and the mixture was further stirred for 6.5 h to afford the corresponding homoallylic amine in good yield along with a minor amount of the homoallylic alcohol.

The generality of the method was also investigated with a variety of alcohols. In all cases the reaction preceded smoothly and good yields of the corresponding homoallylic amines **5** were obtained (Table 4). The present protocol therefore appears to be quite general, atom and pot economical.

The isolation of RCHO, $TsNH_2$, and *N*-tosylaldimine during the reaction provides strong evidence for the reaction pathway proposed in Scheme 2. Details of the mechanism of oxidation of alcohols to aldehydes with chloramine-T[16] and that of indium-promoted allylation of aldehydes and aldimines are available in the literature.[13,17] Probably, the catalyst $FeCl_3$ activates chloramine-T and alcohols through coordination to accelerate their oxidation with chloramine-T. Moreover, indium metal, aldehydes, and aldimines would also be activated by $FeCl_3$ for allylation.

In summary, we have developed a new approach for the synthesis of homoallylic alcohols and amines directly from alcohols. The protocol involves the one-pot $FeCl_3$-catalyzed oxidation of alcohols to aldehydes with chloramine-T followed by indium-mediated Barbier allylation to afford homoallylic alcohols. Similarly, the condensation of oxidation product aldehydes with oxidation by-product *p*-toluenesulfonamide affords *N*-tosylimines, which undergo an indium-mediated Barbier-type allylation with allyl bromide to afford homoallylic amines in the same reaction vessel. Thus, the present work opens up a new and efficient one-pot synthetic route to homoallylic alcohols and amines.

Experimental Section

General Procedure for One-Pot Synthesis of Homoallylic Alcohols 4 Directly from Alcohols

A mixture of alcohol **1** (2 mmol), chloramine-T (2 mmol) and $FeCl_3$ (10 mol%) in 3–5 mL of DCM was stirred at room temperarue for 3–5 h, then indium powder (2 mmol) and allyl bromide **3** (3 mmol) were added. The resultant reaction mixture was stirred for 5–12 h at room temperature. The reaction progress was monitored by TLC. Upon completion (Table 4), the solvent was evaporated under reduced pressure, the residue dissolved in 10 mL THF, the reaction mixture was quenched with saturated ammonium chloride and extracted with diethyl ether (2×10), dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The residue thus obtained was purified by silica gel column chromatography using ethyl acetate-*n*-hexane as eluent to afford an analytically pure sample of **4**.

General Procedure for One-Pot Synthesis of Homoallylic Amines 5 Directly from Alcohols

A mixture of alcohol **1** (2 mmol), chloramine-T (2 mmol) and $FeCl_3$ (10 mol%) in 3–5 mL of dry DCM was stirred at room temperature for 3–5 h followed by addition of 4 Å molecular sieve (200 mg) and stirring for 1–2.5 h at the reflux temperature. Then, the reaction mixture was cooled to room temperature and indium powder (2 mmol) and allyl bromide **3** (3 mmol) were added. The resultant reaction mixture was

stirred for 6–14 h at room temperature. The reaction progress was monitored by TLC. The isolation, purification, and characterization of product **5** were done by following the same procedure as described above for the synthesis of homoallylic alcohols **4**.

The structures of the products were confirmed by comparison of their mp, TLC, IR and ^{1}H NMR data with those of authentic samples obtained commercially or prepared by the literature methods.[13]

Acknowledgements

We sincerely thank SAIF, Punjab University, Chandigarh, for providing microanalyses and spectra. One of us (R.P.) is grateful to the CSIR, New Delhi, for the award of a Senior Research Fellowship.

References

[1] a) J. S. Yadav, B. V. Subba Reddy, G. G. K. S. Narayana Kumar, T. Swamy, *Tetrahedron Lett.* **2007**, *48*, 2205; b) J. S. Yadav, B. V. Subba Reddy, T. Maity, G. G. K. S. Narayana Kumar, *Tetrahedron Lett.* **2007**, *48*, 7155; c) G. G. Launay, A. M. Z. Slawin, D. O'Hagan, *Beilstein J. Org. Chem.* DOI: 10.3762/bjoc.6.41; d) A. P. Dobbs, S. J. J. Guesn, R. J. Parker, J. Skidmore, R. A. Stephenson, M. B. Hursthouse, *Org. Biomol. Chem.* **2010**, *8*, 1064.

[2] W. Li, J. Gan, R. Fan, *Tetrahedron Lett.* **2010**, *51*, 4275.

[3] a) D. T. Hung, J. B. Nerenberg, S. L. Schreiber, *J. Am. Chem. Soc.* **1996**, *118*, 11054; b) R. S. Coleman, J. Li, A. Navarro, *Angew. Chem.* **2001**, *113*, 1786; *Angew. Chem. Int. Ed.* **2001**, *40*, 1736; c) J. D. White, P. R. Blakemore, N. J. Green, E. B. Hauser, M. A. Holoboski, L. E. Keown, C. S. N. Kolz, B. W. Phillips, *J. Org. Chem.* **2002**, *67*, 7750; d) A. B. Smith, C. M. Adams, S. A. L. Barbosa, A. P. Degnan, *J. Am. Chem. Soc.* **2003**, *125*, 350.

[4] a) Y. Ohfune, K. Hori, M. Sakitani, *Tetrahedron Lett.* **1986**, *27*, 6069; b) S. Laschat, H. Kunz, *J. Org. Chem.* **1991**, *56*, 5883; c) L. Graziani, G. Porzi, S. Sandri, *Tetrahedron: Asymmetry* **1996**, *7*, 1341; d) E. Jo, Y. Na, S. Chang, *Tetrahedron Lett.* **1999**, *40*, 5581; e) S. Deloisy, H. Tietgen, H. Kunz, *Collect. Czech. Chem. Commun.* **2000**, *65*, 816; f) D. L. Wright, J. P. Schulte II, M. A. Page, *Org. Lett.* **2000**, *2*, 1847; g) A. D. Jones, D. W. Knight, D. E. Hibbs, *J. Chem. Soc. Perkin Trans. 1* **2001**, 1182; h) F.-X. Felpin, S. Girard, G. Vo-Thanh, R. J. Robins, J. Villieras, J. Lebreton, *J. Org. Chem.* **2001**, *66*, 6305; i) C. O. Puentes, V. Kouznetsov, *J. Heterocycl. Chem.* **2002**, *39*, 595; j) X. Pannecoucke, F. Outurquin, C. Paulmier, *Eur. J. Org. Chem.* **2002**, 995.

[5] a) Y. Yamamoto, N. Asao, *Chem. Rev.* **1993**, *93*, 2207; b) C.-J. Li, *Tetrahedron* **1996**, *52*, 5643; c) D. A. Russo, *Chem. Ind.* **1996**, *64*, 405; d) S. E. Denmark, J. Fu, *Chem. Rev.* **2003**, *103*, 2763; e) J. Podlich, T. C. Maier, *Synthesis* **2003**, 633; f) C.-J. Li, *Chem. Rev.* **2005**, *105*, 3095.

[6] a) J. H. Clark, D. J. Macquarrie, *Handbook of green chemistry and technology*, Wiley-Blackwell, **2008**; b) A. Lapain, D. Constable, *Green Chemistry Metrics*, Wiley-Blackwell, **2008**; c) P. T. Anastas, J. C. Warner, *Green Chemistry: Theory and Practice*, Oxford UK, Oxford University Press, **1998**; d) P. Tundo, A. Perosa, F. Zecchini, *Methods and Reagents for Green Chemistry*, Hoboken NJ, John Wiley & Sons, **2007**.

[7] a) L. Blackburn, R. J. K. Taylor, *Org. Lett.* **2001**, *3*, 1637; b) M. S. Kwon, S. Kim, S. Park, W. Bosco, R. K. Chidrala, J. Park, *J. Org. Chem.* **2009**, *74*, 2877; c) B. Gnanaprakasam, J. Zhang, D. Milstein, *Angew. Chem.* **2010**, *122*, 1510; *Angew. Chem. Int. Ed.* **2010**, *49*, 1468.

[8] a) C. Bolm, J. Legros, J. L. Paih, L. Zani, *Chem. Rev.* **2004**, *104*, 6217; b) C. Pavan, J. Legros, C. Bolm, *Adv. Synth. Catal.* **2005**, *347*, 703; c) M. Nakanishi, C. Bolm, *Adv. Synth. Catal.* **2007**, *349*, 861; d) F. G. Gelalcha, B. Bitterlich, G. Anilkumar, M. K. Tse, M. Beller, *Angew. Chem.* **2007**, *119*, 7266; *Angew. Chem. Int. Ed.* **2007**, *46*, 7134; e) G. Anilkumar, B. Bitterlich, F. G. Gelalcha, M. K. Tse, M. Beller, *Chem. Commun.* **2007**, 289; f) B. D. Sherry, A. Fürstner, *Acc. Chem. Res.* **2008**, *41*, 1500; g) U. Jana, S. Maiti, S. Biswas, *Tetrahedron Lett.* **2008**, *49*, 858; h) X.-F. Wu, D. Bezier, C. Darcel, *Adv. Synth. Catal.* **2009**, *351*, 367; i) L. Ilies, J. Okabe, N. Yoshikai, E. Nakamura, *Org. Lett.* **2010**, *12*, 2838.

[9] a) M. Tandon, P. K. Z. Krishna, *Phys. Chem.* **1985**, *266*, 1153; b) D. Mantzavinos, R. Hellenbrand, A. G. Livingston, I. S. Metcalfs, *Appl. Catal. B: Environ.* **1996**, *11*, 99; c) R. A. Singh, R. S. Singh, *Oxid. Commun.* **1997**, *19*, 248; d) V. Y. Konyukhov, I. V. Chernaa, V. A. Naumov, *Kinet. Catal.* **1997**, *38*, 811; e) M. Navarro, W. F. De Giovani, J. R. Romero, *J. Mol. Catal. A: Chemical* **1998**, *135*, 249; f) M. Hirano, K. Kojima, S. Yakabe, T. Morimato, *J. Chem. Res.* **2001**, 249; g) N. V. Svetlakov, V. G. Nikitin, A. O. Orekhova, *Russian J. Org. Chem.* **2002**, *38*, 753; h) J. K. Joseph, S. L. Jain, B. Sain, *Eur. J. Org. Chem.* **2006**, 590; i) S. Kguchi, T. Kitazume, *Tetrahedron Lett.* **2006**, *47*, 2797; j) N. Jiang, A. J. Ragauskas, *Tetrahedron Lett.* **2007**, *48*, 273.

[10] a) G. Cainelli, G. Cardillo, *Chromium Oxidations in Organic Chemistry*, Springer, Berlin, **1984**; b) K. E. Harding, L. M. May, K. F. Dick, *J. Org. Chem.* **1975**, *40*, 1664; c) J. C. Collins, W. W. Hess, F. J. Frank, *Tetrahedron Lett.* **1968**, *9*, 3363; d) E. J. Corey, J. W. Suggs, *Tetrahedron* **1975**, *31*, 2647; e) K. Omura, D. Swern, *Tetrahedron* **1978**, *34*, 1651; f) P. L. Annelli, F. Montanari, S. Quici, *Org. Synth.* **1990**, *69*, 212; g) M. Frigerio, M. Santagostino, *Tetrahedron Lett.* **1994**, *35*, 8019; h) M. Frigerio, M. Santagostino, S. Sputore, G. Palmisano, *J. Org. Chem.* **1995**, *60*, 7272; i) S. De Munari, M. Frigerio, M. Santagostino, *J. Org. Chem.* **1996**, *61*, 9272; j) M. Frigerio, M. Santagostino, S. Sputore, *J. Org. Chem.* **1999**, *64*, 4537.

[11] a) V. V. Zhdankin, P. J. Stang, *Chem. Rev.* **2002**, *102*, 2523; b) T. Wirth, *Angew. Chem.* **2005**, *117*, 3722; *Angew. Chem. Int. Ed.* **2005**, *44*, 3656; c) U. Ladziata, V. V. Zhdankin, *ARKIVOC* **2006**, 26; d) V. V. Zhdankin, P. J. Stang, *Chem. Rev.* **2008**, *108*, 5299.

[12] a) R. D. Richardson, J. M. Zayed, S. Altermann, D. Smith, T. Wirth, *Angew. Chem.* **2007**, *119*, 6649; *Angew.*

Chem. Int. Ed. **2007**, *46*, 6529; b) J. D. More, N. S. Finney, *Org. Lett.* **2002**, *4*, 3001.

[13] a) D. E. Gremyachinskiy, L. L. Smith, P. H. Gross, V. V. Samoshin, *Green Chem.* **2002**, *4*, 317; b) X.-H. Tan, B. Shen, W. Deng, H. Zhao, L. Liu, Q.-X. Guo, *Org. Lett.* **2003**, *5*, 1833; c) A. Rosales, J. L. Oller-Lo'pez, J. Justicia, A. Gansauer, J. E. Oltra, J. M. Cuerva, *Chem. Commun.* **2004**, 2628; d) P. Sinha, S. Roy, *Organometallics* **2004**, *23*, 67; e) K. Smith, S. Lock, G. A. El-Hiti, M. Wada, N. Miyoshi, *Org. Biomol. Chem.* **2004**, *2*, 935; f) M. K. Chaudhuri, S. K. Dehury, S. Hussain, *Tetrahedron Lett.* **2005**, *46*, 6247; g) K. Surendra, N. S. Krishnaveni, R. Rao, *Tetrahedron Lett.* **2006**, *47*, 2133; h) U. K. Roy, S. Roy, *Tetrahedron Lett.* **2007**, *48*, 7177; i) L. Zhang, Z. Zha, Z. Zhang, Y. Li, Z. Wang, *Chem. Commun.* **2010**, DOI: 0.1039/C0CC01964J; j) L. Zhang, Z. Zha, Z. Wang, *Synlett* **2010**, 1915.

[14] a) L. D. S. Yadav, C. Awasthi, *Tetrahedron Lett.* **2009**, *50*, 715; b) L. D. S. Yadav, R. Patel, V. P. Srivastava, *Synlett* **2008**, 1789; c) L. D. S. Yadav, V. P. Srivastava, R. Patel, *Tetrahedron Lett.* **2008**, *49*, 3142; d) L. D. S. Yadav, C. Awasthi, A. Rai, *Tetrahedron Lett.* **2008**, *49*, 6360; e) L. D. S. Yadav, R. Patel, V. K. Rai, V. P. Srivastava, *Tetrahedron Lett.* **2007**, *48*, 7793; f) R. Patel, V. P. Srivastava, L. D. S. Yadav, *Adv. Synth. Catal.* **2010**, *352*, 1610.

[15] a) B. W. Yoo, J. W. Choi, S. K. Hwang, D. Y. Kim, H. S. Baek, K. I. Choi, J. H. Kim, *Synth. Commun.* **2003**, *33*, 2985; b) B. W. Yoo, S. K. Hwang, D. Y. Kim, J. W. Choi, S. O. Kang, B. S. Yoo, K. I. Choi, J. H. Kim, *Bull. Korean Chem. Soc.* **2004**, *25*, 1633; c) Y. Moglie, F. Alonso, C. Vitale, M. Yus, G. Radivory, *Tetrahedron* **2006**, *62*, 2812.

[16] a) K. N. Vinod, Puttaswamy, K. N. N. Gowda, *Inorg. Chim. Acta* **2009**, *362*, 2044; b) V. Sharma, K. V. Sharma, V. W. Bhagwat, *Eur. J. Chem.* **2008**, *5*, 894.

[17] a) C.-J. Li, *Tetrahedron* **1996**, *52*, 5643; b) S. Kallstrom, T. Saloranta, A. J. Minnaard, R. Leino, *Tetrahedron Lett.* **2007**, *48*, 6958; c) J. Legros, F. Meyer, M. Coliboef, B. Crousse, D. Bonnet-Delpon, J.-P. Begue, *J. Org. Chem.* **2003**, *68*, 6444.

