Metal(II) Schiff base complexes as catalysts for the high-regioselective conversion of epoxides to β-hydroxy nitriles in glycol solvents

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Abstract: A facile preparation of 3-hydroxy propanenitrile derivatives is described involving ring opening of epoxides with potassium cyanide in glycol solvents in the presence of Schiff base complexes as catalysts. This method occurs under neutral and mild conditions with high yields and high regioselectivity. Thus, several β-Hydroxy nitriles, useful intermediates toward biologically-active molecules, are easily obtained at room temperature.

Key words: β-hydroxy nitrile, Schiff base, epoxide, glycol, catalyst.

Résumé : On décrit une préparation facile de dérivés du 3-hydroxypropanenitrile qui implique l'ouverture d'époxydes à l'aide de cyanure de potassium dans des solvants à base de glycol, en présence de complexes de bases de Schiff comme catalyseurs. Cette méthode implique des conditions neutres et douces et conduit à des rendements et une régiosélectivité élevés. Opérant à température ambiante, on an a ainsi préparé plusieurs β-hydroxynitriles utiles comme intermédiaires dans la synthèse de molécules biologiquement actives.

Mots clés : β-hydroxynitrile, base de Schiff, époxyde, glycol, catalyseur.

[Traduit par la Rédaction]

Introduction

β-hydroxy nitriles are important reagents as well as technical products in organic chemistry. They have been extensively investigated and employed for the preparation of intermediates of many naturally occurring bioactive compounds (1–4).

β-Hydroxy nitriles can be prepared by the reaction of epoxides with the toxic volatile HCN (5), NaCN (6, 7), KCN (8), LiCN (9), cyanide exchange resin (10*b*), and TBAF–TMSCN in CH_3CN (11–13). The reaction of epoxides with NaCN, KCN, or HCN usually requires extended times (6, 7*b*, 7*c*, 8*c*), protic solvents (5–7, 8*a*, 8*b*), or additives (7*a*, 8*c*), e.g., Zr-catalyzed one-pot synthesis of β-cyanohydrins from olefins via epoxidation of the olefins and nucleophilic ring opening of the epoxides (10*a*). Some of these reactions afford mixtures of regioisomers (8*c*, 10*b*, 11) or stereoisomers (5). By using trimethylsilylcyanide (TMSCN) in the preparation of β-hydroxy nitriles, the iso-nitrile has been formed (12, 13*d*) as the main product.

In the literature, ring opening of epoxides with cyanide ion as a nucleophile has been carried out by employing nonvolatile alkali cyanides in the presence of perchlorate salts (14) or $Yb(CN)_3$ (12, 14). Some methods employ acetone cyanohydrin in the presence of various bases (15) or lanthanide alkoxides (16), alkyl aluminum cyanides (17), and $Ce(OTf)_4$ (18). In most methods referred to in the literature, the reaction conditions are usually severe; some reagents are commercially unavailable and have to be prepared from alkali cyanides. In addition, the use of alkyl aluminum cyanides presents difficulty in large scale reactions.

To overcome these limitations, we developed a new approach of oxirane ring opening with potassium cyanide in glycol solvents using Schiff base complexes as catalysts at room temperature to afford β-hydroxy nitriles.

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Results and discussion

Metal(II)-salen complexes are promising catalysts for various reactions. These complexes have shown wide applicability and are now used as catalysts for a variety of enantioselective reactions, such as oxidation (19), aziridination (20), cyclopropanation (21), the Diels–Alder reaction (22), and the conversion of 1,2-epoxyethanes to 2-haloethanols with molecular halogen (23).

In this study, the reaction of styrene oxide with potassium cyanide in the presence of some Schiff base complexes of metal(II) was carried out. The preparation and characterization of these complexes were according to the procedure reported in the literature (23–25). On this basis, the syntheses of these metal complexes were essentially the same and involved heating and stirring of stoichiometric amounts of the appropriate tetradentate ligand and metal acetate in a suitable solvent, such as methanol, ethanol, or water–methanol mixtures. The desired complexes crystallized upon cooling and were recrystallized from chloroform. The complexes are easy to prepare and cheap. All of the used metal chelates in this study are insoluble in water but soluble in most organic

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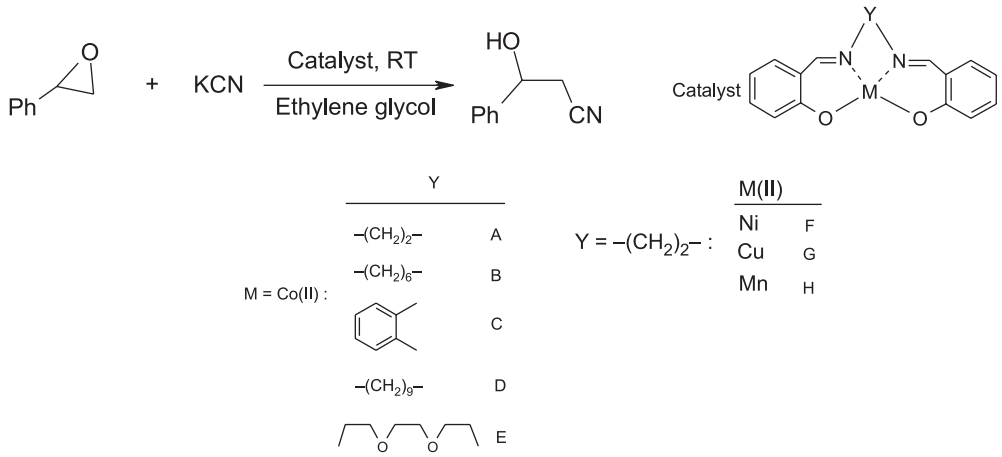
Scheme 1.



solvents. They are stable in water, even at high pH and temperature.

The IR spectrum of the Schiff base exhibits a band at 1625 cm^{-1} assigned to υ(C=N) of azomethine (26). This band shifts to a lower wavenumber by about 10–15 cm^{-1} on the chelation of the ligand with a metal ion. In the ^1H NMR spectra of the Schiff bases (26), the broad signals around 12.5–13.1 ppm are assigned to the protons of the hydroxyl groups in the free ligands. Protons of CH=N have the same chemical shifts (8.5–8.9 ppm). The signal around 6.0–6.65 ppm is assigned to the protons of the NCHN, and signals around 6.6–7.90 ppm are assigned to the protons of aromatic rings (CH=CH). In the ^1H NMR spectra of the Schiff base complexes, all of these signals exhibit a 0.6 ppm shift to a lower field and the broad signal around 12.5–13.1 ppm disappeared. In the IR spectrum, the appearance of two or three bands in the low frequency region (between 420 and 540 cm^{-1}) indicates the coordination of phenolic oxygen in addition to azomethine nitrogen (24).

To examine the effects of the ligands on the catalyst, a variety of ligands were employed in the reaction (Scheme 1).

After a solution of styrene oxide and a catalyst (molar ratio is 10:1) in ethylene glycol was stirred at room temperature, 1.2 mol of potassium cyanide was added to the flask. In this reaction, 3-hydroxy-3-phenyl propanenitrile was obtained as a product and its yield was determined by GC and TLC analysis. The results of the reactions of styrene oxide with potassium cyanide in the presence of the previously mentioned catalysts are given in Table 1.

As shown in Table 1, in these reactions, β-hydroxy nitriles were prepared as products in good to excellent yields with high regioselectivity. In each case, cleavage of the epoxide ring occurs. After completion of the reaction, by addition of water and work-up with CH_2Cl_2, propanenitriles are obtained.

In comparison, the cleavage behaviour of styrene oxide with potassium cyanide in the absence of the catalyst is given in Table 1 (entry 9). This reaction in ethylene glycol in the absence of the catalyst has afforded the product with very low yield and low regioselectivity even with an extended reaction time to overnight. As seen in Table 1, the yields of the reactions with this new method are quite fair, and the reaction time is short. It is of great importance that the reaction is largely affected by the various ligands of the complexes. The complex catalysts **A** and **B** are the most effective ones in these reactions (Table 1, entries 1 and 2), while the complex catalysts **C**, **D**, and **E** have shown lower catalytic performance. This can be related to the low ability of their ligands to coordinate the metal(II) ions.

Table 1. The reaction of styrene oxide with KCN in the presence of various complex catalysts in ethylene glycol.

Entry	Catalyst	Time (h)	Yield (%)[a]
1	A	2.4	98[b]
2	B	2.6	95
3	C	3.0	90
4	D	3.2	88
5	E	3.2	85
6	F	3.8	68
7	G	4.3	63
8	H	4.5	55
9	–	Overnight	20

Note: The reactions were carried out at room temperature.
[a]GC yield based on epoxide.
[b]The only formed *trans*-isomer.

Because H_2-salen is the most effective ligand for the reaction, we studied the catalytic effect of the first-row transition metal(II) with the ligand of *N*,*N*′-ethylenedisalicylideneamine (H_2-salen) on the formation of 3-hydroxy-3-phenyl propanenitrile (Table 1, entries 1, 6, 7, and 8). On the other hand, because the first-row transition metal(II) complexes of simple Schiff base are known to be sparingly soluble in common organic solvents, the different of the used complexes may be attributed to their own solubility or their adducts with epoxide in the reaction solution.

From the previous studies, the Co(II)-salen **A** was the best catalyst used in this reaction (see Table 1). To study the solvent effect on the reaction, nucleophilic cleavage of styrene oxide with potassium cyanide by catalyst **A** has been carried out in various glycol solvents. The results shown in Table 2 indicated that ethylene glycol is the most convenient solvent in this reaction. It was found that these reactions appeared to be largely dependent on the nature of the solvent.

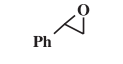
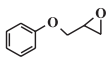
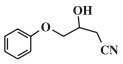
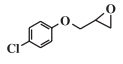
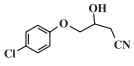
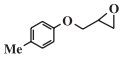
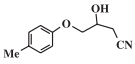
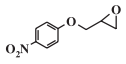
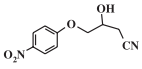
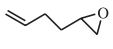
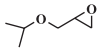
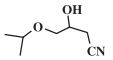
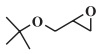
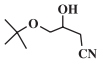
The results of the reactions of some representative

Table 2. Ring cleavage of styrene oxide by KCN in the presence of 0.1 mol of catalyst **A** in various solvents at room temperature.

Entry	Solvent	Time (h)	Yield (%)[a]
1	Ethylene glycol	2.4	98
2	Glycerol anhydrous	2.5	90
3	Triethylene glycol anhydrous	3	75
4	Triethylene glycol dimethyl ether	4	75
5	Tetraethylene glycol	4	65

[a]GC yields.

Table 3. Reaction of various epoxides with cyanide in the presence of 0.1 mol of catalyst **A** in ethylene glycol at room temperature.

Entry	Substrate	Product	Time (h)	Yield (%)[a]
1			2.4	92
2			2.7	90
3			2.8	93
4			2.6	88
5			3.0	93
6			2.2	84
7			2.2	83
8			2.3	80
9			2.5	85
10			2.2	82

[a]Isolated yields based on epoxide.

epoxides in the presence of complex **A** as the catalyst are summarized in Table 3. In these reactions, the optimum amount of the catalyst used for all of the epoxides was 0.1 mol for 1 mol of epoxide. As can be seen, at the same amount of the catalyst, the ring opening of various epoxides have been carried out with 80%–93% yields, and the reaction time was 2.2–3.0 h.

As shown in Table 3 (entry 6, in which only the trans isomer is obtained), the reactions are completely anti-stereoselective. As for the regioselectivity, an attack of the nucleophile preferentially occurs at the less-substituted oxirane carbon. An anti-Markovnikov type regioselectivity is generally observed in these reactions. In many cases, this type of regioselectivity appears to be the opposite of that observed in ring opening of the same epoxides with aqueous hydrogen cyanide under classic acidic conditions. The previously mentioned regiochemical mode can be viewed as occurring via a nucleophilic attack by a cyanide ion on the less sterically hindered oxirane carbon. This mechanism closely resembles the S_N2 model for aliphatic nucleophilic displacement.

The structure of β-hydroxy nitrile products has been assigned by spectroscopic data. In the IR spectra, the C–N stretching vibrations of the nitrile groups appear in the region between 2250 and 2274 cm^{-1}. The hydroxyl group O–H bond stretching frequency is found in the region between 3400 and 3477 cm^{-1} as a strong broad band. The C–H stretching vibrations of the alkyl groups appear in the region between 2877 and 2960 cm^{-1}. In the ^1H NMR spectra, OH protons have chemical shifts between 4.20–4.55 ppm as a singlet broad peak. The signals around 6.5–8.4 ppm are assigned to the protons of CH=CH of the aromatic rings.

Conclusion

This new method for the preparation of β-hydroxy nitriles have some advantages, such as high regioselectivity, high yields, short reaction times relative to other procedures, and work-up simplicity. The nucleophilic attack by the cyanide ion on the epoxides occurs at the primary carbon atom. Thus, we have not so far detected secondary cyano derivatives.

Experimental section

Column chromatography was carried out using 100–200 mesh silica gel (Acme India Ltd., Maharashtra, India). TLC analyses were performed on Merck 60 PF254 silica gel plates. Melting points were determined in open capillaries using an Electrothermal Mk3 apparatus. IR spectra were recorded using a PerkinElmer FT-IR 550 spectrometer and values are reported as υ in cm^{-1}. ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX-400 spectrometer for samples as indicated with tetramethylsilane as internal reference. Mass spectra were recorded on a Finnigan MAT 44S with an ionization voltage of 70 eV. The elemental analyses (CHN) were obtained from a Carlo ERBA Model EA 1108 analyzer carried out on PerkinElmer 240c analyzer.

General procedure for the cleavage of epoxide into β-hydroxy nitriles

To a solution of epoxide (20 mmol) in ethylene glycol (30 mL), KCN (22 mmol) was added and the mixture was stirred for 5 min at room temperature. Then, catalyst **A** (as the modified catalyst) (2.0 mmol) was added, and stirring was continued to completion of the reaction as indicated by TLC. Then, 100 mL water and 20 mL CH_2Cl_2 were added to the reaction mixture while stirring. After being stable, the organic phase was collected and concentrated to dry under reduced pressure. The product was washed with brine and dried over anhyd Na_2SO_4. Evaporation and purification by column chromatography employing EtOAc–hexane (3:7) as the eluent afforded the pure β-hydroxy nitriles.

3-Hydroxy-3-phenylpropanenitrile

Yield: 92%; liquid. IR (Neat, cm^{-1}): 3445, 3062, 3034, 2899, 2255, 1604, 1495, 1456, 1412, 1329, 1204, 1081, 1059, 1028, 940, 867, 757. ^1H NMR (400 MHz, $CDCl_3$) δ: 2.67–2.84 (2H, m), 4.25 (1H, t, J = 5.98 Hz), 4.35 (1H,

br s), 7.35 (5H, m). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 22.8, 69.8, 117.4, 125.5, 128.7, 128.8, 141.1. MS (70 eV): 147 (M^+), 121, 107, 105, 91, 79, 77. Anal. calcd.for C_9H_9NO: C 73.45, H 6.16, N 9.52; found: C 73.17, H 6.13, N 9.24.

3-Hydroxy-4-phenoxybutanenitrile

Yield: 90%; mp 58–61 °C. IR (Neat, cm^{-1}): 3437, 3066, 2930, 2256, 1228, 1047. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.60–2.84 (2H, m), 3.96–4.12 (2H, m), 4.20 (1H, m), 4.35 (1H, br s), 6.77–7.00 (3H, m), 7.14–7.29 (2H, m). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 21.7, 62.5, 69.1, 113.1, 117.1, 126.6, 130.3, 155.8. MS (70 eV): 177, 119, 107, 94, 77.

3-Hydroxy-4-(4-chlorophenoxy)butanenitrile

Yield: 93%; mp 65–68 °C. IR (KBr, cm^{-1}): 3438, 3098, 2879, 2255, 1242, 1092, 1043. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.55–2.67 (2H, m), 3.86–4.07 (2H, m), 4.37 (1H, m), 4.39 (1H, br s), 6.84 (2H, m), 7.24 (2H, m). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 20.6, 64.1, 68.9, 114.4, 115.3, 124.6, 127.3, 154.9. MS (70 eV): 211, 141, 128, 94.

3-Hydroxy-4-(4-methylphenoxy)butanenitrile

Yield: 88%; mp 54–58 °C. IR (Neat, cm^{-1}): 3477, 3028, 2931, 2254, 1193, 1044. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.22 (3H, s), 2.69–2.88 (2H, m), 3.68–3.81 (2H, m), 4.42 (1H, m), 4.54 (1H, br s), 6.73–6.94 (2H, m), 7.06–7.19 (2H, m). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 20.6, 21.3, 67.1, 73.9, 124.6, 116.1, 128.6, 129.1,158.0. MS (70 eV): 191, 139, 108, 91, 77.

3-Hydroxy-4-(4-nitrophenoxy)butanenitrile

Yield: 93%; mp 71–74 °C. IR (KBr, cm^{-1}): 3401, 3023, 2938, 2274, 1240, 1102, 1052. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.43–2.58 (2H, m), 3.78–3.89 (2H, m), 4.30 (1H, m), 4.62 (1H, br s), 7.24 (2H, m), 8.08 (2H, m). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 21.0, 22.5, 68.1, 74.2, 117.7, 125.3, 132.6, 139.1, 155.0. Anal. calcd. for $C_{10}H_{10}N_2O_4$: C 54.06, H 4.54, N 12.61; found: C 54.02, H 4.49, N 12.49.

2-Hydroxy-1-cyclohexanecarbonitrile

Yield: 84%; liquid. IR (KBr, cm^{-1}): 3425, 2960, 2885, 2254, 1189, 1082, 1038, 948, 870, 790. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.2–1.4 (3H, m), 1.7–1.9 (3H, m), 2.15 (1H, m), 2.3 (1H, m), 2.4 (1H, s), 2.5 (1H, m), 3.6–3.8 (1H, m). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 20.6, 23.3, 24.1, 26.9, 33.4, 60.3, 118.6. Anal. calcd. for $C_7H_{11}NO$: C 67.17, H 8.86, N 11.19; found: C 67.05, H 8.81, N 10.94.

3-Hydroxy-6-heptenenitrile

Yield: 83%; liquid. IR (KBr, cm^{-1}): 3401, 3023, 2938, 2274, 1240, 1102, 1052. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.14 (2H, m), 2.41 (2H, m), 2.67–2.85 (2H, m), 3.91 (1H, m), 4.21 (1H, br), 4.87 (1H, dd, J_1 = 9.6 Hz, J_2 = 2.1 Hz), 4.94 (1H, dd, J_1 = 16.3 Hz, J_2 = 2.1 Hz), 5.69 (1H, m). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 28.3, 30.4, 36.3, 66.16, 114.3, 119.8, 137.0. Anal. calcd. for $C_7H_{11}NO$: C 67.17, H 8.86, N 11.19; found: C 67.15, H 8.70, N 11.02.

3-Hydroxy-4-isopropoxybutanenitrile

Yield: 80%; liquid. IR (KBr, cm^{-1}): 3445, 2924, 2899, 2253, 1602, 1495, 1412, 1329, 1028, 868. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.21 (6H, d, J = 6.1 Hz), 2.64–2.75 (2H, m), 3.24 (2H, m), 3.6 (1H, m), 3.7 (1H, m), 3.98 (1H, br). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 21.9, 22.7, 65.3, 70.6, 72.1, 117.8. Anal. calcd. for $C_7H_{13}NO_2$: C 58.72, H 9.15, N 9.78; found: C 58.62, H 9.08, N 9.57.

4-(Tert-butoxy)-3-hydroxybutanenitrile

Yield: 85% ; liquid. IR (KBr, cm^{-1}): 3432, 2933, 2894, 2258, 1594, 1483, 1440, 1354, 1031, 890. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.14 (9H, s), 2.36–2.48 (2H, m), 3.14 (2H, m), 3.88 (1H, m), 4.14 (1H, br). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 22.1, 27.4, 66.5, 68.5, 73.2, 117.8. Anal. calcd. for $C_8H_{15}NO_2$: C 61.12, H 9.62, N 8.91; found: C 62.01, H 9.55, N 8.78.

3-Hydroxybutanenitrile

Yield: 82%; liquid. IR (KBr, cm^{-1}): 3419, 2916, 2887, 2251, 1519, 1474, 1365, 1033, 890, 745. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.74 (3H, d, J = 5.3 Hz), 2.34–2.47 (2H, m), 4.07 (1H, m), 4.25 (1H, br). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 21.6, 25.3, 63.7, 119.0.

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References

1. G. Dittus. *In* Methoden der organishen chemie (Huben–Weyl). *Edited by* E. Mulle. Thieme Verlag, Stuttgart. 1965. p. 451.
2. D.C. Ha and D.J. Hart. Tetrahedron Lett. **28**, 4489 (1987).
3. (*a*) W. Seidel and D. Seebach. Tetrahedron Lett. **23**, 159 (1982); (*b*) A.I. Meyers and R.A. Amos. J. Am. Chem. Soc. **102**, 870 (1980).
4. A. Kramer and H. Pfander. Helv. Chim. Acta, **65**, 293 (1982).
5. (*a*) F. Fülöp, I. Huber, G. Bernáth, H. Hönig, and P. Seufer-Wasserthal. Synthesis, 43 (1991), and refs. cited therein; (*b*) J.G. Smith. Synthesis, 629 (1984); (*c*) W. Nagata, M. Yoshioka, and T. Okumura. J. Chem. Soc. **17**, 2365 (1970).
6. A. Kamal, G.B. Ramesh Khanna, and R. Ramu. Tetrahedron Asymmetry, **13**, 2039 (2002).
7. (*a*) N. Iranpoor, H. Firouzabadi, and M. Shekarize. Org. Biomol. Chem. **1**, 724 (2003); (*b*) A. Kamal and G.B. Ramesh Khanna. Tetrahedron Asymmetry, **12**, 405 (2001); (*c*) O. Pàmies, J.-E. Bäckvall. Adv. Synth. Catal. **343**, 726 (2001).
8. For examples, see: (*a*) J. Jin and S.M. Weinreb. J. Am. Chem. Soc. **119**, 2050 (1997); (*b*) T. Itoh, K. Mitsukura, W. Kanphai, Y. Takagi, H. Kihara, and H. Tsukube. J. Org. Chem. **62**, 9165 (1997); (*c*) M. Chini, P. Crotti, L. Favero, and F. Macchia. Tetrahedron Lett. **32**, 4775 (1991).
9. (*a*) J.A. Ciaccio, C. Stanescu, and J. Bontemps. Tetrahedron Lett. **33**, 1431 (1992); (*b*) J.A. Ciaccio, M. Smrtka, and W. Maio. *In* Proceedings of the 226th ACS National Meeting, New York. American Chemical Society, Washington D.C. 2003. ORGN–123.
10. (*a*) S. Yamasaki, M. Kanai, and M. Shibasaki. J. Am. Chem. Soc. **123**, 1256 (2001); (*b*) B. Tamami, N. Iranpoor, and R. Rezaei. Synth. Commun. **33**, 3153 (2003).
11. H. Konno, E. Toshiro, and N. Hinoda. Synthesis, 2161 (2003).
12. S. Matsubara, H. Onishi, and K. Utimoto. Tetrahedron Lett. **31**, 6209 (1990).
13. (*a*) M.B. Sassaman, G.K.S. Prakash, and G.A. Olah. J. Org. Chem. **55**, 2016 (1990); (*b*) A.E. Vougioukas and H.B. Kagan.

Tetrahedron Lett. **28**, 5513 (1987); (*c*) M. Hayashi, M. Tamura, and N. Oguni. Synlett, 663 (1992); (*d*) K. Imi, N. Yanagihara, and K. Utimoto. J. Org. Chem. **52**, 1013 (1987); (*e*) K. Sugita, A. Ohta, M. Onaka, and Y. Izumi. Chem. Lett. **3**, 481 (1990).
14. M. Chini, P. Crotti, L. Favero, and F. Macchia. Tetrahedron Lett. **32**, 4775 (1991).
15. A. Tsuruoka, S. Negi, M. Yanagisawa, K. Nara, T. Naito, and N. Minami. Synth. Commun. **27**, 3547 (1997).
16. H. Ohno, A. Mori, and S. Inoue. Chem. Lett. 975 (1993).
17. (*a*) W. Nagata, M. Yoshioka, and T. Okumura. Tetrahedron Lett. 847 (1966); (*b*) J.C. Mullis and W.P. Weber. J. Org. Chem. **47**, 2873 (1982).
18. N. Iranpoor and M. Shekarriz. Synth. Commun. **29**, 2249 (1999).
19. (*a*) T. Katsuki. J. Mol. Catal. A, **113**, 87 (1996); (*b*) E.N. Jacobsen. *In* Catalytic asymmetric synthesis. *Edited by* I. Ojima. VCH Publishers Inc., New York. 1993. pp. 159–202.
20. (*a*) T. Katsuki, K. Noda, N. Hosoya, and R. Irie. Synlett, 469 (1993); (*b*) T. Katsuki and H. Nishikori. Tetrahedron Lett. **37**, 9245 (1996); (*c*) T. Katsuki, K. Hori, H. Sugihara, and N. Ito. Tetrahedron Lett. **40**, 5207 (1999).
21. (*a*) T. Katsuki and T. Fukuda. Synlett, 825 (1995); (*b*) T. Katsuki and T. Fukuda. Tetrahedron, **53**, 7201 (1997); (*c*) T. Katsuki, T. Uchida, and B. Saha. Synlett, 114 (2001).
22. T. Katsuki and Y. Yamashita. Synlett, 829 (1995); (*b*) E.N. Jacobsen, J. Branalt, and S.E. Schaus. J. Org. Chem. **63**, 403 (1998).
23. H. Sharghi and H. Naeimi. Bull. Chem. Soc. Jpn. **72**, 1525 (1999).
24. (*a*) R.H. Holm, G.W. Everett, and A. Chakravorty, Jr. Prog. Inorg. Chem. **7**, 83 (1966); (*b*) B. Mahapatra and D. Panda. Transition Metal. Chem. (London), **9**, 280 (1984).
25. H. Naeimi. Ph.D. thesis, Shiraz University, Shiraz, Iran. 1997.
26. H. Sharghi and H. Naeimi Khaledi. Iran. J. Chem. Chem. Eng. **18**, 72 (1999).